July, 1933

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

VOLUME VI NUMBER 3

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RUBBER CHEMISTRY AND TECHNOLOGY

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Vol. VI July, 1933 No. 3

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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New Books and Other Publications

Thirteenth Report on Native Rubber Cultivation, Fourth Quarter, 1932. Prepared by the Bureau of Agricultural Economics of the Division of Agriculture of the Netherland Indian Department of Agriculture, Industry & Commerce at Buitenzorg, Java. Paper cover pamphlet; 19 pp. For free distribution.

This is a general review of the rubber market in Java containing tables and graphs showing the export of native rubber and price course at Tapanoeli, monthly export of native rubber (dry) from the Outer Provinces, and the export of native rubber from the Outer Provinces. [From the *Rubber Age of New York.*]

Rubber Producing Companies. Compiled by the Mincing Lane Tea & Rubber Share Brokers' Association, Ltd. Published by "The Financial Times," Ltd., 72 Coleman St., London, E. C. 2, England.

This standard work follows the lines of previous editions. The authentic and exhaustive information given concerns over 600 planting companies and includes capital, acreage, latest accounts, crops, purchase price, dividends, forward sales, estimates, etc. Particulars are given of many companies with tea and coffee interests, also a list of directors and secretaries of rubber companies. [From the *India Rubber World.*]

Hard Rubber Compounding, Laboratory Report No. 163, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. This report from the Organic Chemicals Department of the du Pont Rubber Laboratory differentiates between "hard rubber" and "ebonite," outlines the methods of vulcanization used, tabulates the effect of loading on allowable steam pressure for non-blowing cure, and discusses the effect of various pigments including zinc oxide, etc. Practical formulas are given for various black hard rubber articles and for colored hard rubber stocks. [From the *India Rubber World.*]

Rubber-Soled and Rubber Footwear, Report No. 63, second series, prepared by the United States Tariff Commission to the President. 1933. For sale by the Superintendent of Documents, Washington, D. C. Price 5 cents. Paper cover pamphlet; 22 pp.

This pamphlet contains the United States Tariff Commission report to the President on the differences in costs of production of rubber-soled and rubber footwear in the United States and in the principal competing countries as ascertained pursuant to the provisions of Section 336 of Title III of the Tariff Act of 1930. Included, also, is an appendix proclamation by the President. [From the *Rubber Age of New York.*]

Digest of Patents Dealing with Rubber and/or Latex in Road Construction Materials (Excluding Blocks). Technical Research and Development of New Uses Committee of The Rubber Growers' Association, Inc., 2, 3, and 4 Idol Lane, Eastcheap, London, E. C. 3, England. Sections of this digest are devoted to: preparation of purely bituminous emulsions; compositions containing latex or raw rubber plus bitumen, etc.; compositions containing vulcanized rubber and bitumens, etc.; compositions containing latex or raw rubber and cements, etc.; various compositions not necessarily bituminous; methods of attachment to surfaces, etc. This digest should prove of assistance to those who require a handy reference of the patent literature of the subject. [From the *India Rubber World.*]

Annual Survey of American Chemistry. Vol. VII, 1932, Edited by Clarence J. West. Foreword by Charles A. Kraus, chairman, Division of Chemistry and Chemical Technology. Published for National Research Council by The Chemical

Catalog Co., 330 W. 42nd St., New York, N. Y. 1933. Cloth, 340 pages, 5 by $8^1/_4$ inches. Author and subject indices. Price $4.00 net.

In this volume, as in that for 1931, a full review of rubber research for 1932 is given by John T. Blake, research chemist, Simplex Wire & Cable Co., Boston, Mass.

The topics covered are chemistry and structure, electrical properties, vulcanization, accelerators, antioxidants, latex, pigments and compounding, testing and control, manufacturing processes, and a few miscellaneous references of scientific interest. [From the *India Rubber World.*]

Handbook of Chemistry and Physics. A Ready Reference Book of Chemical and Physical Data. Seventeenth Edition, 1932. Editor in Chief, Charles D. Hodgman. Chemical Rubber Publishing Co., 1900 W. 112th St., Cleveland, O. Flexible leather, 1722 pages; $4^1/_8$ by $6^3/_4$ inches. Price $6.

In the preparation of the seventeenth edition the "Handbook of Chemistry and Physics" has been subjected to an unusually extensive revision. A very large number of tables have been revised and enlarged. Material covering more than 300 pages in the sixteenth edition has been extensively changed involving an increase of over 100 pages. Wholly new material has been added.

The most important revision is that of the table "Physical Constants of Organic Compounds" which has been completely recompiled and is now presented in new form. This new table of Organic Compounds, covering 220 pages, was compiled with the assistance of 125 professors of organic chemistry and a number of directors of commercial research in this country. The data for every compound have been carefully revised and more than 1000 new compounds added because of their commercial importance and value in teaching or in research.

A considerable addition has been made to the mathematical section of the book, including a very complete collection of "Integrals" and extensive "Interest Tables." The sections devoted to "Heat of Formation and Solution" and to "Vapor Pressure" also have been completely revised. A new and very complete table of "Magnetic Susceptibility" has been added. [From the *India Rubber World.*]

"Chemical Guide Book." 1933. Ninth Edition. Chemical Markets, Inc., 25 Spruce St., New York, N. Y. Cloth, 600 pages, 4 by 9 inches.

This trade annual is a complete directory and buyers' guide for those interested in purchasing supplies of chemicals. The work comprises 5 divisions, as follows: Part I, Catalog of leading chemical firms arranged alphabetically; Part II, Buying guide and directory; Part III, Geographical directory of the chemical and allied trades; Part IV, Buyers' guide on containers, packing, and shipping supplies; and Part V, Chemical statistics.

A valuable feature is the brief descriptive item under each material listed covering its chemical and physical properties and manufacturing uses. [From the *India Rubber World.*]

Index to A.S.T.M. Standards and Tentative Standards, issued by the American Society for Testing Materials, Philadelphia, October, 1932. Paper cover. 119 pp.

This booklet comprises a valuable reference to Specifications, Methods of Testing, Recommended Practices, Definitions of Terms, Charts and Tables of A.S.T.M. Standards. Under the heading of Rubber Products are listed specifications for the various rubber products for which specifications are available, such as, hose, cotton goods, friction tape, gloves, insulated wire and cable, matting and pump valves. [From *The Rubber Age of New York.*]

Standards Yearbook 1933. Compiled by United States Bureau of Standards, United States Department of Commerce. Washington, D. C., Government

Printing Office. 250 pages and index. For sale by the Superintendent of Documents, Washington, D. C. Price $1.00.

This, the seventh edition, is full of suggestions and data for all engaged in standardization. It is a standardization reference book, summarizing current standardization activities and outstanding accomplishments during the year. The activities and accomplishments of not only the bureaus and agencies of the Federal government, but also those of states and counties are outlined. The book contains a résumé of the standardization work of scientific and technical societies and trade associations. A brief account of international coöperation in standardization is followed by a summary of the activities of the national standards associations of the various countries. This volume informs the manufacturer of the current standardization movements affecting his industry. It informs the purchasing agent of new standard specifications, and the scientist engaged in research as to current research projects which may lead to standardization. [From the *India Rubber World.*]

American Standards Year Book, 1932–1933 edition, published by American Standards Association, New York City, $7^3/_4 \times 10^1/_2$ in., 48 pp.; paper cover; issued May 8, 1933.

The establishment during the past 12 months of 31 new national industrial standards affecting the construction, electrical, mining, oil, steel, radio, and almost every other major American industry is recorded in this report for 1932–33. The Year Book is issued as a record of the coöperative achievement of nearly 3000 scientists and engineers representing more than 500 national technical and trade organizations in the development of a unified system of basic technical standards for industry. It reveals that this work, which was started in 1918, has gone on without abatement during the past few years despite the depression.

Among some of the new national standards listed are those for inch-millimeter conversion for industrial uses; specifications for impregnated paper insulation for lead-covered power cables; abbreviations for technical terms; engineering charts for lantern slides; requirements for flexible gas tubing and many others. [From *The Rubber Age of New York.*]

Handbook of Industrial Temperature and Humidity Measurement and Control. By M. F. Behar. Instruments Publishing Co., Pittsburgh, Pa., 1932. Cloth. $6 \times 9^1/_4$ in. 320 pp. 278 illustrations. $4.00.

Two separately titled books are here combined into one volume, namely, "Temperature Measurement and Control" and "Humidity Measurement and Control." These constitute, respectively, Part Two and Part Three of the Manual of Instrumentation which the author undertook several years ago with the purpose of laying the foundation of a modernized form of industrial engineering.

The book deals with subjects of prime importance to industry: (1) Thermometry. (2) Pyrometry. (3) Automatic control of temperature. (4) Humidity measurement and control.

Of the two chapters which pertain to the four major subjects, first is a general discussion of temperature. It opens with the aspect of temperature as an industrial service condition, deals with measurement principles, describes the International Temperature Scale and classifies industrial temperature instruments. The other general chapter is on temperature recorders. Free from theory, it describes many types, including those brought out in 1932, and discusses the advantages and limitations of all types of mechanical and electrical instruments.

This work supplies up-to-date information on hundreds of instruments and formulates many principles of measurement and control, the application of which are of practical value in all industries. [From *The Rubber Age of New York.*]

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 8, No. 4, pages 364–389, December, 1932.]

Studies in the Interfacial Relationships between Rubber and Fillers

I. The Tear-Resistance of Vulcanized Rubber

G. Lefcaditis (Athens), and F. H. Cotton

Department of Chemistry and Rubber Technology, Northern Polytechnic, London, England

Part I—Examination of Testing Methods

The remarkable increase in the wearing capabilities of vulcanized rubber rendered possible during the last decade by compounding the unvulcanized material with certain finely divided fillers, in particular an amorphous carbonaceous soot of extreme subdivision known as carbon black, has received considerable attention from both chemists and physicists. Various theories have been advanced to explain this reinforcement of rubber by finely divided pigments, but at present it is widely believed that interfacial energy effects are mainly responsible.

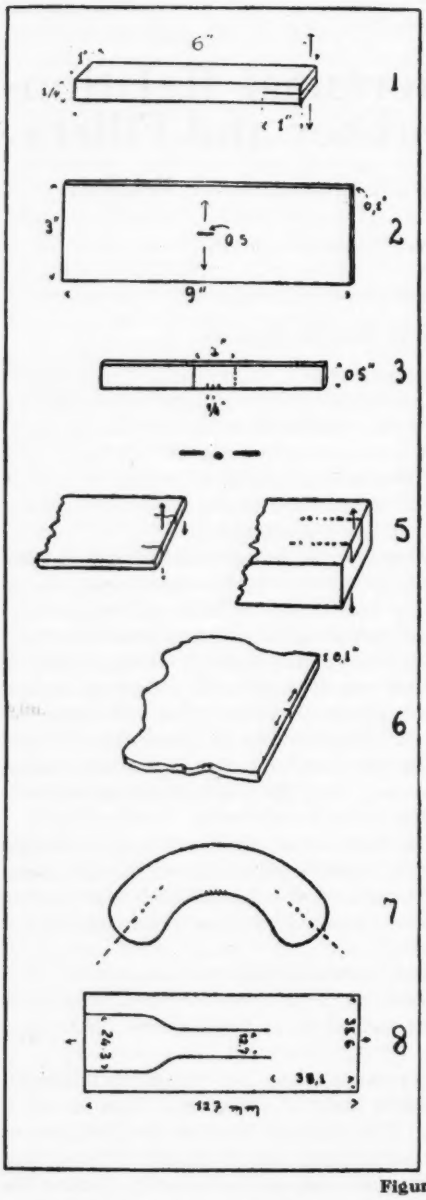
There are, however, certain significant facts which, though not overlooked, have hitherto not been satisfactorily explained by surface energy conceptions. Foremost among these is that of two fine powders such as carbon black and refined china clay, both of which are capable of greatly increasing the ultimate tensile strength of vulcanized rubber; the former gives a product highly resistant to tear, while the latter produces a vulcanized rubber which can be torn with comparative ease. It has been assumed that the anomalous behavior of carbon black and china clay can be attributed to geometrical anisotropy of the particles of clay contrasted with those of gas black, the suggestion being that the sharp edges of the plate-like microcrystals of clay cut into the rubber. However, other fillers of anisotropic character do not give the same poor resistance to tear.

The technical importance of tear tests will be evident when the proved influence of tear-resistance on the wearing properties of stretched vulcanized rubber is emphasized. Tests designed to measure the resistance of vulcanized rubber to tearing were first introduced ten years ago, and a summary of those since suggested is given in the following pages.

It will be evident from a perusal of these methods that the tests hitherto employed were mainly of an empirical character, and this must be attributed to experimental difficulties in measuring resistance to tear as distinct from other characteristics of rubber.

It will be noted that tests so far employed fall into two categories; namely, those in which tear-resistance is measured in terms of energy and those in which the resistance is stated in terms of force. If an analysis be made of either type of test, it will be clear that there is a partition of force, and of energy, between true tearing and stretching of the rubber. Furthermore, in the majority of cases the path and extent of the tear are profoundly influenced by the shape and size of the test-piece, by its elastic characteristics, and by the form of the cut from which initial tearing proceeds.

In fact, on account of the complexity of the phenomenon of tearing it has proved exceedingly difficult to measure tear-resistance with the accuracy of other physical testing methods. Little has been studied systematically, and the results published



1. Evans, B. B.

Test-piece slowly torn on the dynamometer and load causing continuous tearing noticed, as well as length of tear and appearance of graph.

2. Zimmerman, E. C.

Test-piece torn for a certain length in continuation of the central slit by pulling of hooks on a tester, at speed 2–6 inches per min.

Tear-resistance expressed as energy absorbed.

3. Tuttle, J. B.

Test-piece torn on tester and the elongation of a length initially 1 inch taken as tear-resistance.

4. Marzetti, B.

Test-piece similar to Evans' cross-section, 10 × 10 mm. (see Fig. 1, No. 1).

5. Heathcote, H. T.

Method similar to above.

6. Dinsmore, R. P., Zimmerman, A. O.

Subjective method, to be used comparatively. Test-piece is torn by hand.

7. Ayres, H. D. (Winkelmann, H., Goodrich).

Test-piece torn on a tester at 20 inches per min. speed. Maximum load taken as tear-resistance and expressed in lb. per unit thickness.

8. Wright, D. D.

Test-piece pulled and torn on a tester, and combined results obtained for tensile and shearing.

Figure 1

are difficult to compare on account of the essentially different conditions under which they were obtained.

In the desire to apply the most accurate testing method it was found necessary to examine most of those described in the literature, and a short description of them and their chief characteristics is given with explanatory diagrams (Figs. 1 and 2).

9. Laboratories of the Goodyear Co., U. S. A.

High speed tear. Test piece torn on a Cooey test machine modified. Speed 20 inches per min. Maximum load at complete tearing taken as tear-resistance and expressed in kg. required to tear this test-piece.

10. Laboratories of the Goodyear Co.

Laminated tear. Test piece fastened on Cooey machine and torn for a certain length. Tear-resistance calculated according to Zimmermann's formula and expressed as kg. cm. per sq. cm. Speed 24 inches per min.

11. Heidensohn

Test-piece is torn on the testing machine. Tear-resistance calculated from the maximum load to tear Expressed in kg. per cm.

12. Present Writers

Test-piece is torn on the Scott testing machine. Tear-resistance calculated from the average load effecting tearing. Expressed in kg. per cm.

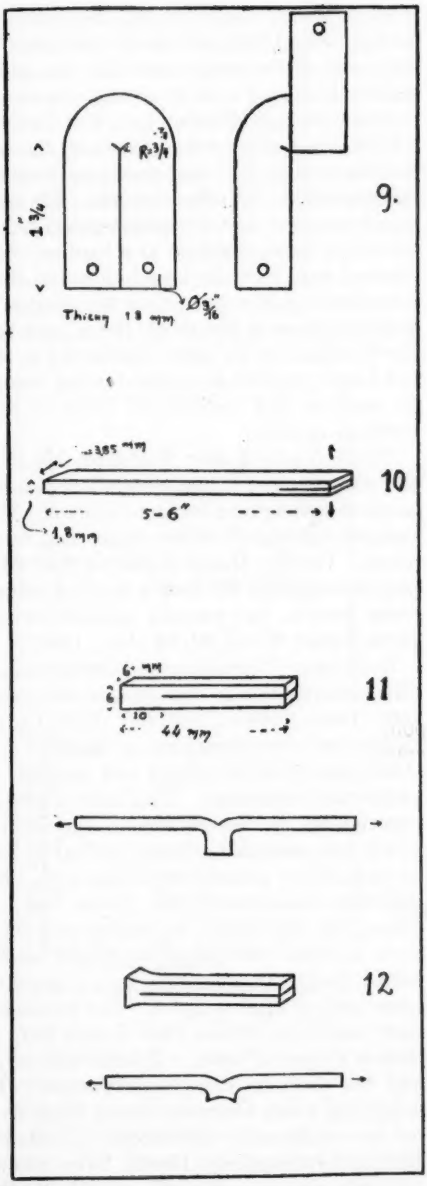


Figure 2

Evans seems to have been the first to publish work on tearability [*India Rubber J.*, **64**, 815 (1922)]. He used a press-moulded test-piece (Fig. 1) and determined the load required to produce continuous tearing. As a result he found a relationship between tear-resistance and "optimum cure," and determined the tearability caused by certain fillers. He did not find any differences due to grain effect.

Pickles [*India Rubber J.*, **67**, 69, 101 (1924)] criticized the way of preparing the test-piece and believed that Evans probably measured ply-separation. This is not the authors' experience, but the size and shape of the test piece allows factors to enter which lead to inconsistent results.

Zimmermann [*Rubber Age (New York)*, **12**, 130 (1922); *India Rubber J.*, **64**, 475 (1922)] devised a method based on the calculation of the energy required to effect tearing, and proved that maximum tear-resistance coincided with "optimum cure" as determined by other criteria. He also found that mineral fillers reduced the tear-resistance as the volume-percentage increased. For mixes of zinc oxide, a minimum tear-resistance at a loading of seven volumes occurred. Zimmermann's method appears to be based on sound theoretical grounds. In performance, however, tearing does not follow the desired direction and usually occurs at an angle with the plane of the sheet, the surface produced by tearing being thus wider than the thickness of the sheet considered in the formula. In repeating his work it was not found possible to obtain tearing across the grain-direction. Others have tried to improve the method by using more convenient test-pieces (see Goodyear's methods below).

Tuttle [*India Rubber World*, **67**, 150 (1922)] proposed a simple method based on the measurement of the elongation of a nicked rubber strip when stretched to the point of tearing on a testing machine. The method does not take into account the varying rigidity of rubber mixes and consequently can only be used with similar mixes. Greider [*India Rubber World*, **23**, 501 (1923)] in a summary of the above papers suggested devising a method using a sharpened wedge to promote tearing. Some have in fact recently carried out work on these lines [Igmanson and Gray, *India Rubber World*, **82**, 82 (July, 1930)].

Luttringer [*Caoutchouc et Gutta-percha*, **20**, 11, 733 (1923)] in a similar survey directed attention to the influence of carbon black and of aging on tearing. Marzetti [*India Rubber J.*, **65**, 691 (1923)] gave an analysis of the phenomenon and by theoretical considerations he deduced a close relationship between the stress-strain properties of rubber and tearing. He considered tearing as a sequence of elementary breakings. Heathcote [*India Rubber J.*, **69**, 143 (1925)] described some experiments on tear-resistance started in 1908. He used two test-pieces, one of which was essentially similar to that of Evans. The tear-resistance was expressed as strength in pounds per linear inch. In performance this method involved the difficulty encountered with Evans' test. Dinsmore and Zimmermann [*Ind. Eng. Chem.*, **18**, 144 (1926)], in dealing with the effect of accelerators on cure, etc., based some of their conclusions on results obtained by a hand-tearing method. They found that tear-resistance was a sensitive criterion of cure particularly when measured on aged samples. The method was mentioned again in detail by Dinsmore and Vogt [*Trans. Inst. Rubber Ind.*, **4**, 85 (1928)] as suited to distinguish the best of a series of cures. For the sake of completeness this test has also been tried and the authors' statements verified. The sensitiveness of such a simple test satisfying most technical needs explains why objective methods have hitherto not been sufficiently developed. (Neither the U. S. A. Bureau of Standards nor the Materialprüfungsamt, Berlin, have adopted any tear test among their rubber-testing methods.) Winkelmann [*India Rubber World*, **79**, 75 (Oct., 1928)] gave a short description of a method developed in the United States, known also as "crescent" or "Goodrich" method. The test-piece has a crescent shape and is die-cut from a sheet about 0.1 in. thick. Five nicks are made by special equipment along the middle of the inner curved surface, and the test-piece is torn on the usual testing machine. While the present investigation was in progress a paper by Carpenter and Sargisson [*Proc. Am. Soc. Testing Materials*, **2**, 897 (1931)] appeared

giving a critical review of the method and results obtained with it. The resistance to tear is calculated as the maximum load registered by the testing machine and expressed as pounds pull per 0.1 inch thickness of the test-piece. The Goodrich method offers certain advantages over previous methods, and has in fact been applied to some extent in rubber laboratories. It is mentioned again in the discussion following. Wright [*Ind. Eng. Chem.*, Anal. Ed., 1, 17 (1929)] described a new physical test for rubber combining a tensile and shear test. This method may be a convenient technical test, but as Memmler and Schob state (Memmler, *Handbuch der Kautschukwissenschaft*, p. 677), it is doubtful whether it gives a clear insight to tearing. Heidensohn (Memmler, *loc. cit.*, p. 676) has carried out some work on the tearability of carbon black mixes, using a test-piece 6 × 6 × 44 mm. taken from the waste center disc of the ring tensile test-piece. The test-piece is cut lengthwise in the middle up to a point 1 cm. from the end, and this end part is torn on the dynamometer.

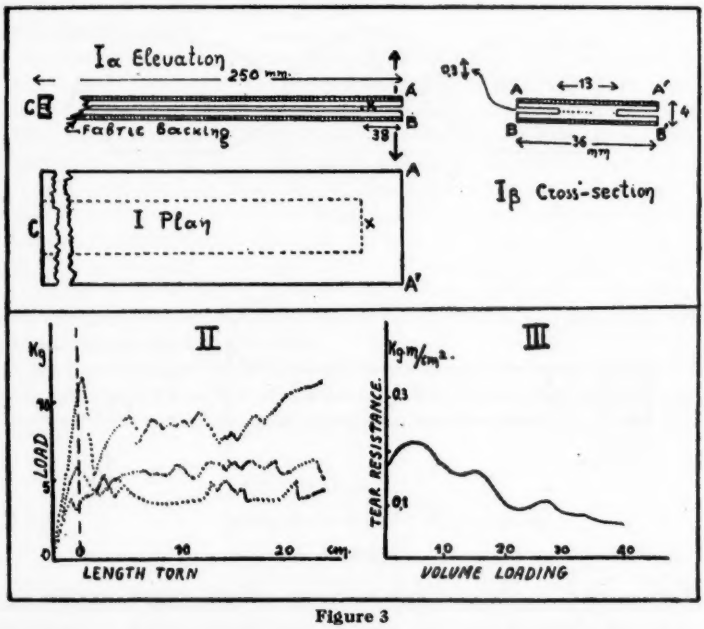


Figure 3

Unpublished Methods.—Dinsmore, of the Goodyear Co., has recently communicated several further, hitherto unpublished methods, two of which, with his kind permission, are described in the table of testing methods. Results obtained in Goodyear's laboratories by these methods are discussed later.

Methods Attempted by the Present Writers.—The figures obtained for tear-resistance by the above methods being much less consistent than those of other standard physical tests on rubber, an attempt was made to develop some other method and test-piece which would give more reliable results. Space does not permit description of all the methods and the test-pieces tried and discarded. One method consisted in measuring the energy required for tearing at high speed, and an impact pendulum was used with certain corrections on the figures obtained. This method was not advanced beyond the experimental stage, but may be used to study the

tearing at very high speed if a more suitable test-piece be devised. Another method was tried on the ordinary dynamometer and the test-piece consisted of a rubber strip 21 cm. long, vulcanized in a special mold, which gave to it the section shown in I.B. (Fig. 3). The two wide flaps on either side of the section to be torn were backed with rubberized fabric during vulcanization. The two ends of the test-piece A, A′ and B, B′ were then gripped in the clamps of a Schopper dynamometer and pulled slowly so that the test-piece tore along the line X–C. The fabric backing prevented elongation of the torn pieces and ensured that no energy was absorbed in stretching the sample. The tear-resistance was measured in terms of energy required to tear the piece, and is expressed in kg. m. per sq. cm. Parallel tests on rubber of the same composition and cure showed discrepancies, as indicated in the three graphs of Fig. 3 (from a vulcanized compound containing 30 volumes of clay) and the explanation was clear after examining the torn section. Tearing did not occur regularly along the plane anticipated. As a result the graph (see III

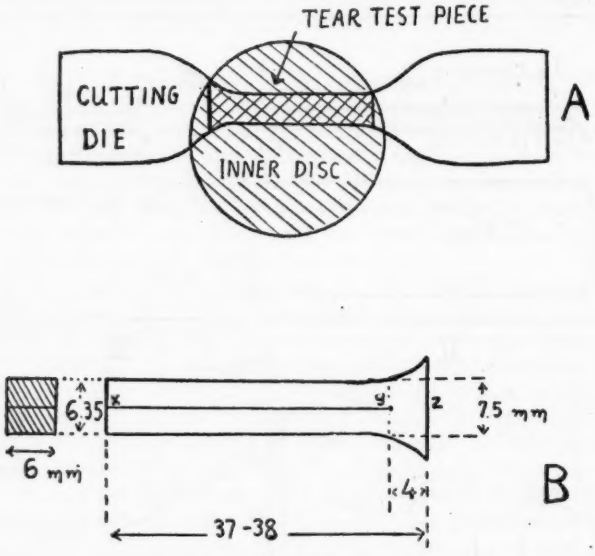


Figure 4

in Fig. 3) obtained for tear-resistance of a series of vulcanized samples containing increasing volume loading of a filler shows irregularities which are not indicated by a similar graph given by an improved method developed later. The above described test-piece as well as the majority of those mentioned in other methods are of comparatively large size, and from personal observations it appears that the greater the dimensions of a test-piece the greater are the probabilities of irregular tearing and non-repeatable results. The majority of factors which interfere with the consistency of the results are of a fortuitous nature, and are connected with the distribution of forces about the tearing plane. These factors can to some extent be controlled by a suitable design of the test-piece, and the method next described partially overcame the difficulty.

Method Adopted.—The test-piece is taken from the inner disc of a 6 mm. Schopper ring, similarly to Heidensohn's test. It is cut by means of the standard dumbbell die adopted by the American Chemical Society [RUBBER CHEM. & TECH., **3**, 179

(1930)]. The resulting butt-ended test-piece is marked as shown at B in Fig. 4 and slit along the middle up to a distance of 4 mm. from the end. For standard working, a simple ink-marking tool was made, and the middle cut carried to the mark by a razor blade.

The two wings of the test-piece are attached to the clamps of a Scott tester and the remaining 4 mm. is torn. The object of the enlarged end of this test-piece was to constrain the tear to occur in the desired direction, *yz*, namely, along the continuation of the line *xy*. It was found as a result of extensive experiments that this enlargement invariably had the desired effect. The torn surface was remarkably flat.

Tearing on the dynamometer at a speed of 20 in. per min. or less, usually occurs in two or three steps, with increasing indications on the dial. The first jerky movement of the dial hand corresponds to the commencement of tearing and is taken as the initial reading, while the highest indication on the dial is obtained when complete tearing of the piece is nearly achieved. The mean of the initial and the final dial readings is taken as the "tearing load," and calculated in kg. per cm. thickness of the test piece.

When particularly smooth-tearing rubbers are tested and the commencement of tearing is not clearly shown by the jerk of the dial hand, it is desirable to have two observers, one of whom watches the test piece while the other records the load.

The Effect of the Length to Be Torn on (a) the Initial, (b) the Final, and (c) the Mean Load Required to Tear.—If the butt-ended test-piece developed by the writers is compared with that used by Heidensohn (see Nos. 11 and 12 of Fig. 2) it will be noticed that in addition to modifying the shape of the end to be torn the length of tearing has been restricted to a distance of 4 mm. as compared with 10 mm. The reason for thus shortening the length to be torn was that in a series of tests using different lengths of tail it was repeatedly noticed that within limits the shorter the distance undergoing tearing, the more closely did the initial and final load registered on the dynamometer tend to coincide.

This is demonstrated in Table I, in which are given the initial and final tearing loads obtained from butt-ended test-pieces cut from a vulcanized compound containing carbon black and china clay, when the length of tearing varied from 2 to 6 mm.

TABLE I

Length of the End-part in Mm.	Tearing Loads in Kg. per Cm. for Butt-ended Test-pieces							Mean Load	
2	Initial..	4.48	4.25	4.50	4.36	4.50	4.32	4.40	4.59
	Final...	4.97	4.63	4.79	4.65	5.21	4.42	4.78	
4	Initial..	3.60	3.72	3.74	3.14	3.45	3.31	3.50	4.40
	Final...	5.40	5.26	5.30	5.43	5.18	5.29	5.30	
6	Initial..	3.94	3.87	3.64	3.44	3.27	3.25	3.57	4.52
	Final...	5.36	6.02	5.75	5.46	5.20	4.97	5.47	

It will be noticed that the mean of the initial and final load is in each case approximately the same, though as indicated in the graph (Fig. 5) the initial load required to promote tearing increased slightly with decrease in length of tail, while the final load proportionally decreased. It was found that the 4 mm. length gave the most consistent and reliable results. A more detailed discussion of the principles underlying the method is given in the following section.

Characteristics of the Method.—The method described has the following characteristics. It is carried out by the standard laboratory equipment, and the results

expressed in metric units. It enables measurements to be made on pure gum mixes which are difficult to examine by other methods.

In tests with non-grained rubbers the tearing occurs regularly along the test-piece and the fresh surface is nearly flat, depending on the mix and the cure. This is of course also the case with pieces cut along calender grain. When the test-pieces are cut across the grain, in some cases (clay mixes; low volume loadings of other fillers) tear occurs neatly across, and the registered pull is distinctly higher than when parallel to the grain. In other cases, however (carbon black and high volume loadings of other fillers), tear occurs sideways and follows the direction of the grain, making impossible any "across" determination. As regards the consistency of the results obtained by the method, it should be noticed that in a series of increasing volume loadings or in a series of cures, the figures for individual test-pieces from, for example, a 30-minute cure, sometimes coincide with figures of individual tests from, for instance, the 35-minute cure, but the average of six test-pieces from each cure gives points which when plotted produce a reasonably regular curve.

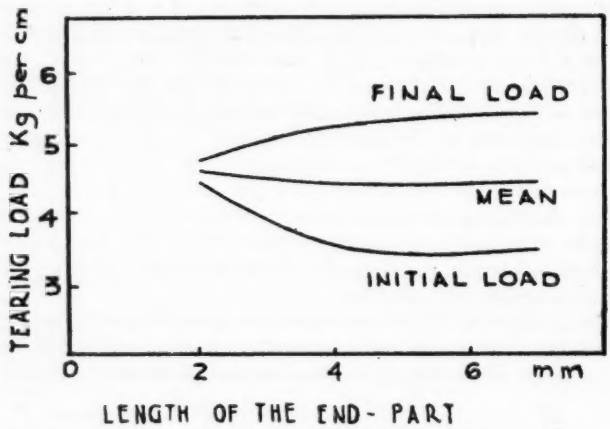


Figure 5—Effect of Tearing Length of a Butt-ended Test-piece, on the Tearing Load

The following numerical examples further illustrate the consistency of the tests with rubber mixes of widely differing character. Figures are kilograms per cm. This table is given only as an indication of the consistency of the readings under various conditions. Comparative data about fillers are given later, together with full details of the mixes, etc.

TABLE II

PURE GUM MIX AT OPTIMUM CURE

Initial...	2.39	2.56	2.40	2.48	2.57	2.56
Final....	4.25	3.72	3.72	3.87	4.17	4.42

20 VOLUMES ZINC OXIDE MIX, OVERCURED

Tearing parallel to the grain. No tear across grain obtainable

Initial...	3.97	4.54	4.22	4.22	3.78	3.96
Final....	8.34	9.45	7.30	9.50	7.07	7.95

20 Volumes Clay Mix at Optimum Cure

Parallel to grain

Initial...	1.17	1.14	1.17	1.29	1.08	1.16
Final....	2.29	2.48	2.28	2.33	2.29	2.25

Across grain

Initial...	1.80	1.67	1.47	1.58	1.53	1.63
Final....	2.39	2.48	2.41	2.55	2.46	2.51

GOODRICH — Tests A + C.

BUTT ENDED — Test by Authors B + C′

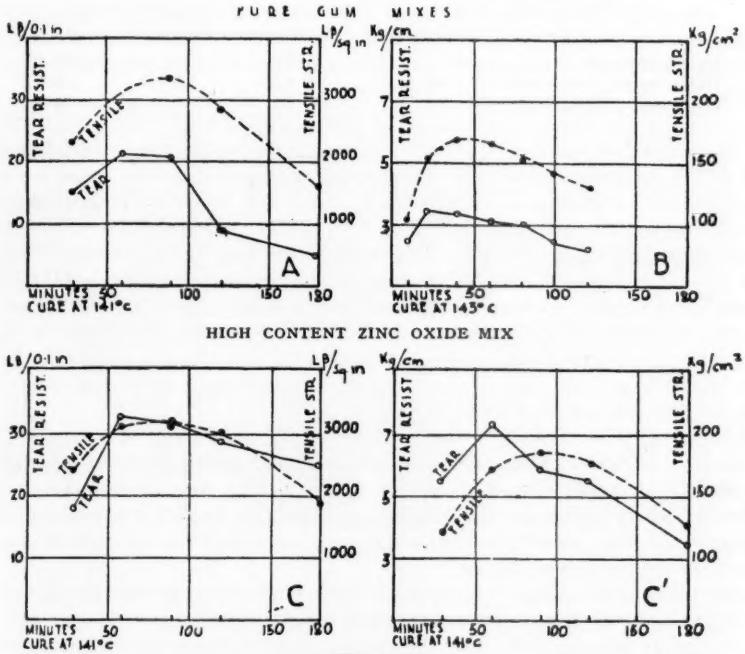


Figure 6

Figure 6 represents the relationship between tear-resistance and time of vulcanization for two types of mix. For comparison, data obtained on standard mixes by Carpenter and Sargisson with the Goodrich method are also given.

The mixes were as follows:

A.—Pure gum mix: rubber (crepe and smoked sheets, 1:1) 100, sulfur 6, zinc oxide XX red 5, hexamethylenetetramine 1.

Data by Carpenter and Sargisson by Goodrich method.

B.—Pure gum mix: rubber (crepe and smoked sheets, 1:1) 100, zinc oxide W. S. 5, ethylidene-aniline condensation product (A. 19) 1, sulfur 3.5.

Data by present writers by butt-ended test-piece.

C.—High zinc oxide mix: rubber (crepe and smoked sheets, 1:1) 100, sulfur 6, zinc oxide XX red 137, hexamethylenetetramine 1.

Data by Carpenter and Sargisson by Goodrich method.

C′.—Same high zinc oxide mix.

Data by present writers, by butt-ended method.

Note.—In comparing the results obtained by the two methods described, it should be noted that the two sets of graphs are in different units. It was felt unwise to convert the figures determined by Carpenter and Sargisson to the metric system because their tensile tests were made by the dumb-bell method, while the authors' were carried out by the ring method, and experience shows that dumb-bell figures are higher.

Comparison of Results Obtained by Different Methods.—An attempt was made to compare results obtained by various methods by expressing them in the same units; *i. e.*, kg. per cm., calculated on the original thickness of the test-pieces (Table III).

TABLE III

	Heidensohn	Goodrich	Goodyear High-speed	Butt-ended Method
Pure gum mix.....	...	25–35	...	4–5
High carbon black mix....	16–22	85–120	25–50	15–17
High zinc oxide mix.....	...	40–55	...	6–8

If the graphs obtained by Carpenter and Sargisson using the Goodrich method (Fig. 6) are compared with those obtained by the present writers using the butt-ended test-pieces described, a similarity in shape will be noticed. Both methods indicate a maximum resistance to tear shortly before the peak of the curve relating tensile strength to time of cure. Nevertheless the figures for the same mix and state of cure expressed in the same units differ essentially (see Table III). Notwithstanding the fact that some difference might be anticipated on account of the different thickness of the test-pieces (as this is the general experience in tensile tests) it is believed that the divergences in question are of much higher order, and must be attributed not only to the thickness but mainly to the shape of the test-piece and the manner of effecting tearing.

Much thought was given to the possibility of a mathematical analysis of the distribution of forces about the plane along which tearing eventually proceeds; but all such attempts proved abortive. It was finally decided that the simplest method by which to examine the distribution about this plane was to make enlarged replicas of the test-pieces with a pattern of squares, and follow the distortion of the pattern on stretching the rubber.

In the photographs (Fig. 7), the test-pieces shown were made from the same stock and vulcanized together, and were stretched to an elongation proved by a previous test on similar samples to be near the tearing point. Hence the distortion visible in the photographs gives a true indication of the relative stresses operative within each square, both in the Goodrich and the butt-ended test-piece.

In the Goodrich test-piece, despite its curvature, there is an almost even distribution of the pulling force throughout the section of the strip when stretched. Consequently only a small part of the pull is concentrated at the tearing line, and the pull required to tear the piece is far higher than it would be if a greater proportion of the load acted through the line at which tearing occurs. With test-pieces in which the pulling force is mostly concentrated across the tearing line, figures obtained are much lower than in the Goodrich test.

Whereas quantitatively, results by various methods differ widely, there is a qualitative agreement which justifies the use of any one for technical purposes. There is, however, a real need for a standard test, and it has already been indicated why the results obtained by means of the butt-ended test-pieces may be considered as more logically representing true resistance to tear.

Nevertheless each method offers some individual performance characteristics which should be mentioned.

The Goodrich method of tearing rubber under considerable strain throughout the test-piece possesses a sensitiveness toward the state of cure which is not shown by other methods to the same extent. The method described in this paper has the advantage of consistency, and consequently enables one to study the variation of tear-resistance caused by small additions of fillers. It is particularly well adapted to the investigation of pure gum mixes and those of low volume loadings.

Grain Effect and Tear-Resistance.—It has already been noticed that previous investigators attempted to measure tear-resistance both parallel to and across the grain of calendered rubber, and figures have been given for the resistance across the grain. Carpenter and Sargisson (*loc. cit.*), however, could not clearly measure the tear-resistance across, because tearing always occurred parallel to the grain.

The experience of the present writers is the same with the majority of test-pieces examined; tearing mostly follows the direction of least resistance, that is, parallel

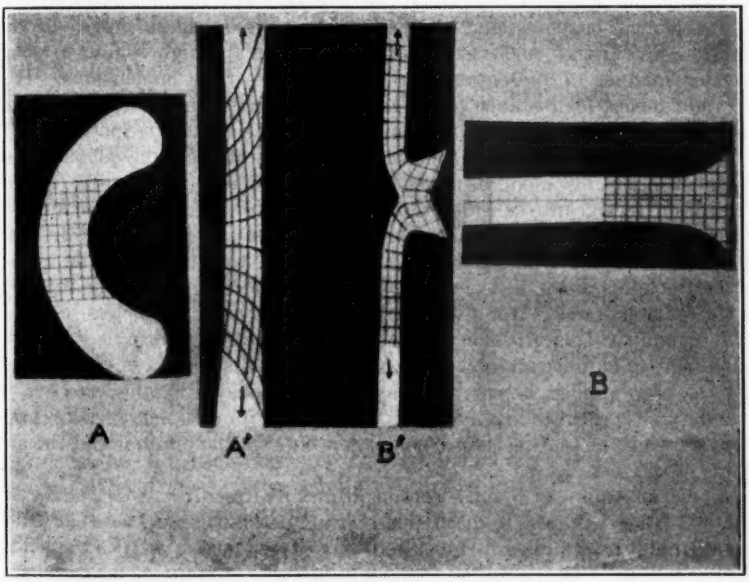


Figure 7

to the grain. An exception has been noticed in certain cases, as described above, by the use of the butt-ended test-piece, whereby some measure of control of the direction of tearing is obtainable. In these cases, the direction of tearing proceeds clearly across the grain and the tear-resistance is higher than the resistance parallel to it. The question therefore arises as to whether one should take as tear-resistance the figure obtained parallel to the grain (Dinsmore, *loc. cit.*), or whether it be preferable to employ test-pieces free from grain. Measurements with grained test-pieces (parallel) have undoubtedly the advantage of more regular tearing, resulting in improved consistency. It may be objected, however, that the extent of calender grain, being exceedingly difficult to reproduce at the same degree throughout a series of measurements, will necessarily affect the resistance to tear. Therefore it has been considered more advisable in the present investigation to work with non-grained test-pieces. The procedure applied to destroy grain is standard practice

in laboratories and consists briefly in plying up the sheets at right angles, warming the rubber before the application of the pressure, and allowing a certain overflow when molding. [Scott, *Trans. Inst. Rubber Ind.*, **5**, 149 (1929), discussion; W. de Visser, "The Calender Effect and the Shrinking Effect of Unvulcanized Rubber," **1926.**]

Effect of Elongation.—In all the previous methods of testing described above, the tear-resistance is expressed in terms of load per unit width, or energy per unit surface calculated on the original dimensions of the test-piece. This is being conventionally adopted in rubber tensile tests, and gives, as far as the stress-strain characteristics of rubber are concerned, clear information. Whenever a calculation on the actual section of the test-piece at any point of strain is desired, this can easily be deduced by the simple relationship between elongation and cross-section, on the assumption that no volume changes take place.

The calculation of tear-resistance on the original width of the test-piece is sufficient for technical purposes, and especially when tests on similar mixes are made. In a large series of mixes, however, including pure gum and high volume loadings of fillers, this manner of presentation might lead to wrong conclusions. Highly loaded rigid mixes, for instance, undergo little change in thickness when stressed to tearing, whereas pure gum compounds show a considerable reduction of thickness. As a result, the actual load per unit thickness at the moment of tearing is much higher in soft, low modulus mixes than in tough ones.

In the desire to take into consideration a correction for this, it has been found that no indirect deduction of the actual thickness of the test-piece could be derived from other characteristics (modulus, etc.) of the mix, as is the case in tensile tests, because the thickness of the test-piece depends, when tearing, on the rigidity as well as on the tear-resistance. From two mixes of similar rigidity the less resistant to tear will undergo less deformation when submitted to tearing stress.

Consequently, a direct method of measurement of the thickness at the point of tearing has been applied, namely, by traveling telescope with calibrated eye-piece scale, and graphs are given in a later part of the paper for complete series of volume loadings showing the tear-resistance calculated both on the original and the actual thickness of the test-pieces.

At the recent American Symposium on Abrasion [*Proc. Am. Soc. Testing Materials*, **2**, 942 (1931)], Amon, in discussing tearing methods, suggested that interesting results might be obtained if elongation were determined as well as the load acting during tearing. In the authors' opinion, however, the direct measurement of the width of the tearing plane is preferable to calculation from a knowledge of the elongation characteristics, because the tearing forces are concentrated at the point of rupture with consequent exaggerated local deformation (see Fig. 7).

Effect of Temperature and Speed.—The effect of temperature on the tear resistance of rubber has not yet been systematically examined. Its determination involves a correction due to the change of the rigidity of rubber as described above. Therefore it is considered necessary to work at constant temperature in the testing room. With regard to the influence of speed, the same reservation holds, and so far attempts to determine tear-resistance at low *versus* high speeds have not proved successful. Hence in the present work 20 in. per min., the standard speed of the testing machine, has been adopted. In cases, however, of mixes with fibrous ingredients, lower speeds may be recommended.

Part II—The Tear-Resistance of Rubber Compounded with China Clay

The properties of china clay as a rubber filler have been examined by several investigators mainly with a view to determine the tensile characteristics which

it imparts to rubber [Wiegand, *India Rubber J.*, **60**, 379, 423 (1920); North, *India Rubber World*, **63**, 98 (1920); Greider, *Ind. Eng. Chem.*, **14**, 385 (1922); Drakeley and Pollett, *Trans. Inst. Rubber Ind.*, **5**, 424 (1929); Dawson, *Trans. Inst. Rubber Ind.*, **1**, 359 (1926); Lunn, *Trans. Inst. Rubber Ind.*, **5**, 396 (1929)], and as a result it has been established that from the point of view of increasing the resilient energy of rubber, refined clay must be placed among the most energetic reinforcing fillers. It remains, however, a matter of experience that clay, though increasing tensile strength of rubber, decreases at the same time its resistance to tear. It has been repeatedly said that this fact is due to the acicular and lamellar shape of the clay particles, which causes a pronounced grain in the rubber, and this explanation has been considered so convincing that little interest has hitherto been shown in the determination in quantitative terms of the influence of clay on the tear-resistance of rubber.

The fact that magnesium carbonate, being a reinforcing filler of pronounced acicular particle shape, does not decrease tear-resistance of rubber to the same extent as clay, may be considered an indication of the insufficiency of the above explanation for the peculiar behavior of clay.

The object of the present paper is systematically to investigate this behavior, considering the influence of clay on rubber throughout a large range of volume-loadings and under various conditions of cure.

Experimental Details.—As the details of experimental procedure are of utmost importance in rubber-testing, it must be emphasized that throughout this work the standard procedure in mixing was that adopted by the American Chemical Society [RUBBER CHEM. & TECH., **3**, 179 (1930)]. Further, as clays are fillers of natural occurrence and widely differing character and properties, it was considered advisable to use a standard grade of highly refined colloidal clay, the reinforcing properties of which have already been investigated (Drakeley and Pollett, *loc. cit.*). This clay (Stockalite) shows a remarkable reinforcement and comparatively little accelerator-absorption.

Tensile strength determinations, wherever mentioned in this paper, have been made on the Schopper ring test-pieces, 6 mm. thick.

Tear-resistance has been measured by the method described in the first part of this work. The six test-pieces were cut from the inner discs of the 3 test-rings which showed closest tensile strength values. The disc of the fourth ring was kept for supplementary test in case of uncertainty.

Preliminary Experiments.—A set of tests has been made to determine the extent to which tear-resistance of a clay mix is influenced by the vulcanizing conditions. This test necessarily involved an examination of several accelerators and a comparison of the effect of high *versus* low temperature cure.

The method of making the test was as follows: To batches of a base mix containing 20 volumes of clay and the zinc oxide necessary for activation, different amounts of sulfur and various accelerators were mixed, as indicated in the adjacent table (No. IV). The accelerators used represented typical classes. In addition, some combinations of accelerators were used on account of their advantages with absorbing fillers. Three temperatures were employed, namely, 125.5° C., 143° C., and 147° C. Each of the accelerators was tried at the temperature at which, according to previous experience, it was known to give the best physical properties. The ratio of accelerator and sulfur to rubber was adjusted to give the maximum tensile strength within the range of the three periods of cure applied to each set.

The object of this procedure was to use every accelerator under the conditions which favor the development of its desired properties. In one case the effect of an antioxidant was also determined.

TABLE IV

Base mix = rubber: (crepe and sm. sheets, 1:1) 100; clay, 56; zinc oxide, 5

	Accelerator, etc.	Amount of Accelerator on Rubber, %	Sulfur on Rubber, %	Temperature	Minutes' Cure
1.	Diphenylguanidine	0.9	3.8		
2.	Ethylidene-aniline condensation product	1.4	3.5	147° C.	20.25.30
3.	Diphenylguanidine + aldol-α-naphthylamine	0.9 + 1	3.8		
4.	Mercaptobenzothiazole + stearic acid	0.8 + 1	3		
5.	Dinitrophenyldimethyldithiocarbamate	0.6	3		
6.	Butyraldehyde condensation product + diphenylguanidine	0.8 + 0.2	3	143° C.	17.23.28
7.	Litharge + lead benzoate	10 + 1	4.5		
8.	Zinc pentamethylenedithiocarbamate + diphenylguanidine	0.5 + 0.3	2	125.5° C.	10.15.20
9.	Tetramethylthiuram monosulfide	0.4	2.2		

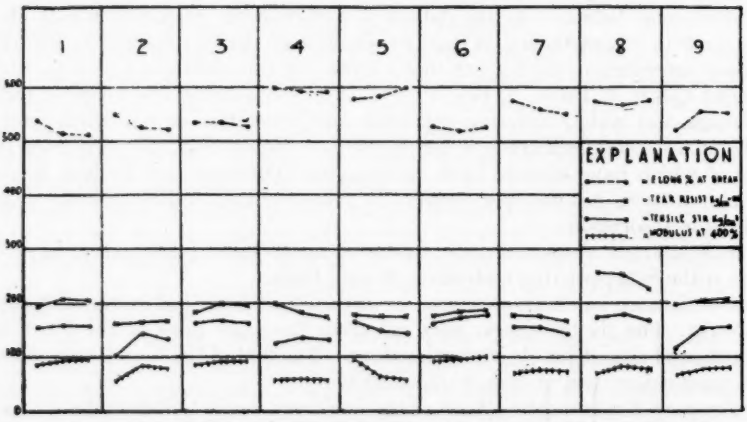


Figure 8—The Influence of Accelerators on the Physical Properties of a Vulcanized Mix Containing 20 Volumes of China Clay (See Table 5)

The results of these tests are given both in Table V and in graphs (Fig. 8) and lead to the following conclusions:

Low-temperature accelerators used with low percentages of sulfur increase the tear-resistance of rubber mixes. No close relationship can be derived between the tensile strength or the modulus of the mixes examined and their respective tear-resistance. A mercaptobenzothiazole mix, showing low modulus, and a diphenylguanidine mix showing a comparatively high modulus gave, however, both approximately the same tear-resistance. It must nevertheless be noticed that for the same mix there was a relationship between tear-resistance and tensile strength if compared over a range of different curing times.

The highest tear-resistance of the 20 volumes clay mix was obtained by the combination of zinc pentamethylenedithiocarbamate and diphenylguanidine. The lowest values were given by the mix accelerated by the ethylidene-aniline condensa-

tion product. The use of an antioxidant gave no noticeable effect. This however does not exclude possible influence in other circumstances. (Severe overcures, aged rubber, etc.)

The Tear-Resistance of Rubber-Clay Mixes over a Range of Volume Loadings.—The preliminary experiments having clearly shown that the tear-resistance of the mixes containing 20 volumes clay was greatly influenced by the conditions under which they had been vulcanized, it was decided to determine the tear-resistance of a series of mixes of increasing volume loading, beginning with a pure gum mix and rising to a highly compounded mix.

A combination of zinc pentamethylenedithiocarbamate and diphenylguanidine in conjunction with a low temperature cure having given high tear-resistance, the mixed accelerators were employed in the series just mentioned. Incidentally, a second series was carried out with an accelerator of the Schiff base type, which gave poor results in the preliminary experiments.

The results of these experiments are summarized in Tables VI and VII and illustrated in graphs (Fig. 9).

An examination of the graphs (Fig. 9), plotted from the maximum tear-resistance measured (which normally occurred before the maximum tensile strength), leads to the conclusion that short cures at low temperature give higher tear-resistance, both with pure gum and clay mixes.

The tear-resistance of both the series of vulcanized rubber-clay mixes examined decreased essentially as the volume-loading of clay increased up to 15 to 20 volumes of clay on 100 volumes of rubber. Beyond this concentration, there was a certain increase in tear-resistance to be noticed in the graph taken with the high-temperature accelerator (A), whereas with the low-temperature accelerator (combination B), the respective tear-resistance does not appreciably change (see Fig. 9).

It may be noted that the lowest tear-resistance was attained at the volume-loadings which give the maximum tensile reinforcement.

The slight upward tendency of the graph at high volume-loadings deserves attention, be-

TABLE V

MECHANICAL PROPERTIES OF A MIX CONTAINING 20 VOLUMES OF CLAY, WITH VARIOUS ACCELERATORS AND TEMPERATURES OF CURE

Temperature of Vulcanization	Time in Min.	Tensile Strength	Elongation	Modulus at 400%	Tear-Resistance
			1		
147° C.	20	158	540	86	1.94
	25	160	518	93	2.06
	30	159	512	95	2.05
			4		
143° C.	18	128	600	55	1.98
	23	34	596	58	1.82
	28	132	593	54	1.73
			8		
125.5° C.	10	171	576	71	2.56
	15	178	571	82	2.50
	20	168	575	72	2.23

Temperature of Vulcanization	Time in Min.	Tensile Strength	Elongation	Modulus	Tear Resistance
			2		
147° C.	20	102	550	55	1.60
	25	144	528	83	1.62
	30	134	523	80	1.65
			5		
143° C.	18	164	580	95	1.78
	23	150	586	64	1.75
	28	145	600	58	1.75
			9		
125.5° C.	10	117	520	67	1.97
	15	152	554	77	2.05
	20	155	552	79	2.07

Temperature of Vulcanization	Time in Min.	Tensile Strength	Elongation	Modulus at 400%	Tear Resistance
			3		
147° C.	20	164	536	86	1.81
	25	169	536	91	1.96
	30	164	530	92	1.94
			6		
143° C.	18	164	527	92	1.82
	23	171	520	96	1.82
	28	178	526	100	1.85
			...	...	....
125.5° C.	10	...	...	...	....
	15	...	...	...	....
	20	...	...	...	....

Temperature of Vulcanization	Time in Min.	Tensile Strength	Elongation	Modulus at 400%	Tear Resistance
			7		
147° C.	20	...	...	...	...
	25	...	...	...	...
	30	...	...	...	...
		155	561	74	1.75
143° C.	18	155	561	74	1.75
	23	142	552	71	1.66
	28				
		...	...	...	...
125.5° C.	10	...	...	...	...
	15	...	...	...	...
	20	...	...	...	...

cause the adverse effect of clay might be expected to continue at higher volumes.

An explanation of this effect seems to be that, at these high loadings, rubber merely acts as a binding medium between the bulk of the clay particles, and the re-

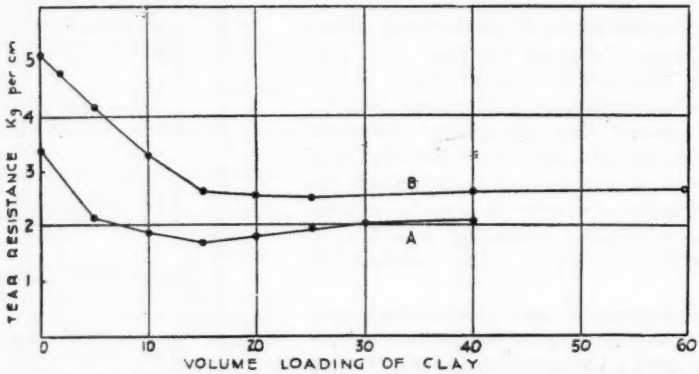


Figure 9—A = Ethylidene-Aniline Condensation Product at 143° C. B = Zinc Pentamethylenedithiocarbamate + Diphenylguanidine at 125.5 °C.

sistance opposed to tearing is probably due to the anchorage of the particles to each other.

The graph obtained from the low-temperature accelerator has been replotted in Fig. 10, with the purpose of showing the form of the variation of the tear-resistance of the series of volume loadings when tear-resistance is calculated on the real

TABLE VI

MECHANICAL PROPERTIES OF A SERIES OF MIXES CONTAINING VARIOUS VOLUME-LOADINGS OF CLAY IN RUBBER WITH COMBINATION OF ZINC PENTAMETHYLENEDITHIO-CARBAMATE AND DIPHENYLGUANIDINE, CURED AT 125.5° C.

Base mix: Rubber (crepe + sheets, 1:1), 100; zinc oxide, 5; Z.P.D., 0.5; D.P.G., 0.3; sulfur, 2

Time of Vulcanization	Tensile Strength	Elongation at Break	Modulus at 400%	Tear-Resistance, Kg. per Cm.	Tensile Strength	Elongation at Break	Modulus at 400%	Tear-Resistance, Kg. per Cm.	Tensile Strength	Elongation at Break	Modulus at 400%	Tear-Resistance, Kg. per Cm.
		Base Mix				2 Vol.				5 Vol.		
5′	175	810	16	4.20	194	800	19.2	4.60	200	750	26.9	4.22
10′	198	780	21.1	5.13	210	745	26.4	4.83	216	725	33.3	4.25
15′	201	726	25.4	4.30	209	710	32	4.20	227	690	41	4.25
20′	187	726	25.7	4.10	210	700	32.4	4.25	216	680	40.2	4.00
		10 Vol.				15 Vol.				20 Vol.		
5′	186	704	39	3.02	176	652	48	2.31	157	560	59	2.27
10′	226	676	46.3	3.30	192	620	59	2.66	171	575	71	2.56
15′	235	644	58	3.26	190	605	71	2.53	178	571	82	2.50
20′	223	646	54	2.94	185	620	63	2.50	168	576	72	2.23
		25 Vol.				40 Vol.				60 Vol.		
5′	130	520	71	2.42	102	440	76	2.40	...	...	..	..
10′	160	545	83	2.53	112	450	92	2.60	56	390	..	2.65
15′	166	527	89	2.53	114	447	93	2.54	62	345	..	2.61
20′	156	540	82	2.46	108	450	90	2.50	67	345	..	2.53

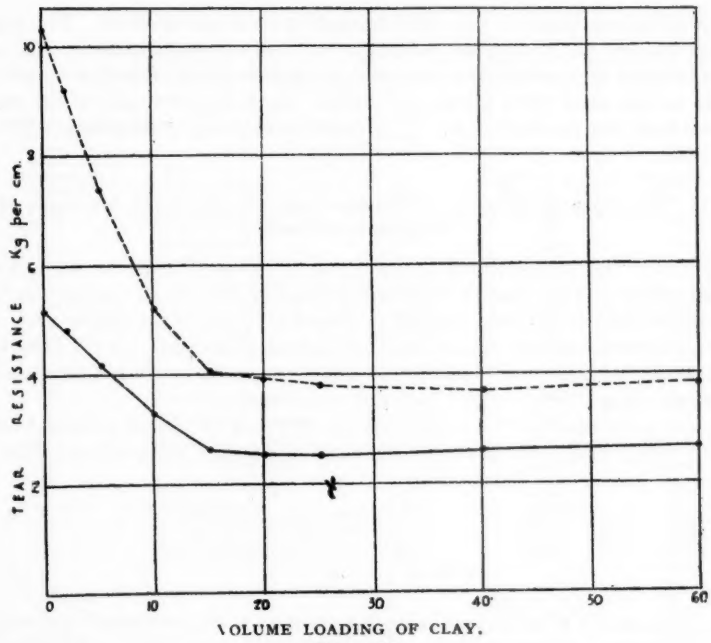


Figure 10

——— = Calculated on the original thickness of the test-piece.
- - - - = Calculated on the real thickness of the test-piece at the point of tearing.

thickness of each test-piece at the point of tearing. In this form of the graph, the tear-resistance of the pure gum mix is much higher than that of the clay compounds,

TABLE VII

MECHANICAL PROPERTIES OF A SERIES OF MIXES CONTAINING VARIOUS VOLUME-LOADINGS OF CLAY IN RUBBER, WITH ETHYLIDENE-ANILINE CONDENSATION PRODUCT, CURED AT 143° C.

Base mix: rubber (crepe + sheets, 1:1) 100; zinc oxide, 5; ethylidene-aniline condensation product, 1; sulfur, 3.5

Time of Vulcanization	Tensile Strength	Elongation at Break	Tear-Resistance, Kg. per Cm.	Tensile Strength	Elongation at Break	Tear-Resistance, Kg. per Cm.	Tensile Strength	Elongation at Break	Tear-Resistance, Kg. per Cm.	Tensile Strength	Elongation at Break	Tear-Resistance, Kg. per Cm.
	Base Mix			5 Vol.			10 Vol.			15 Vol.		
20′	151	836	3.40	129	750	2.11	125	697	1.67	129	658	1.58
40′	171	800	3.33	160	720	2.14	165	683	1.78	137	626	1.53
60′	166	770	3.08	154	716	2.11	162	675	1.80	140	620	1.48
80′	152	767	3.00	145	715	2.08	156	676	1.78	120	592	1.50
100′	137	760	2.50	143	715	2.00	155	680	1.80	114	590	1.56
		20 Vol.			25 Vol.			30 Vol.			40 Vol.	
20′	83	535	1.89	104	553	1.65	65	487	2.03	...	...	..
40′	118	556	1.77	118	514	1.72	92	494	1.92	63	396	1.95
60′	125	570	1.73	121	530	1.86	106	500	1.92	75	400	2.11
80′	120	554	1.73	117	514	1.85	106	494	2.02	132	391	2.04
100′	107	536	1.64	112	520	1.87	103	484	1.94	137	392	2.33

and the initial additions of clay seem to exert a pronounced effect. The end part of the graph does not show much difference by this new representation.

This method of representing the results suggested determination of the effect of small additions of other fillers, and carbon black appeared one of the most interesting from this point of view. The results of such an investigation will be published later.

Part III—The Tear-Resistance of Rubber Compounded with Mixtures of Clay and Carbon Black

This part of the work forms a contribution to the study of the action of blended fillers in rubber. The effect of mixtures of fillers on the tensile strength and other properties of rubber has been studied by Dawson [*Trans. Inst. Rubber Ind.*, **1**, 359 (1926)], and mentioned by Somerville [*Trans. Inst. Rubber Ind.*, **6**, 137 (1930)].

The properties imparted to rubber by a mixture of fillers are not necessarily the mean of the properties given by each filler separately.

The tear-resistances of vulcanized mixes containing two fillers have not hitherto been compared with those of corresponding compounds containing each filler separately.

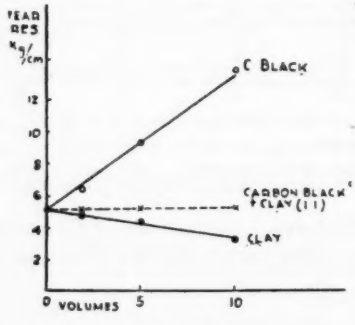


Figure 11

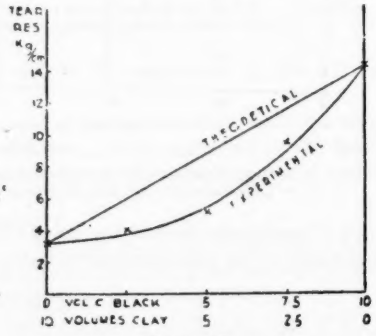


Figure 12

The problem was attacked in the following ways:

(*a*) Measurements of the tear-resistance of a constant volume-loading (10 volumes per 100 vol. of rubber) of either of the two components separately and of their mixtures.

(*b*) Measurement of the tear-resistance of vulcanized compounds containing a series of increasing volume-loadings of the two fillers separately and a series containing increasing volume-loadings of the mixture in the ratio 1:1.

The results are given in Tables VIII and IX, and graphs (Figs. 11 and 12). For the sake of brevity the figures for the optimum time of vulcanization only, chosen from a range of four cures, are given.

It is evident from the two graphs (Figs. 11 and 12) that the tear-resistance of rubber compounded with mixtures of china clay and carbon black is less than would be anticipated from the law of averages.

The results of the present investigation tend to indicate the use of low-temperature vulcanization and short cures to increase the tear-resistance of clay compounds.

Preliminary experiments have shown that rubber highly resistant to tear can be produced by compounding it with china clay, while in the form of latex, and experimental data will be published later.

TABLE VIII

MECHANICAL PROPERTIES (AT THE OPTIMUM VULCANIZATION) OF A SERIES OF MIXES WITH VARIOUS QUANTITIES OF INDIVIDUAL FILLERS AND THEIR MIXTURES. CURED AT 125.5° C.

Base Mix: rubber (crepe + smoked sheets, 1:1) 100; zinc oxide, 5; Z.P.D., 0.5; D.P.G., 0.3; sulfur, 2

Volumes of Fillers	Properties	Clay	Clay + Carbon Black (1:1)	Carbon Black
0	Tensile strength	198	198	198
	Elongation	780	780	780
	Modulus at 400%	21.1	21.1	21.1
	Tear-resistance	5.13	5.13	5.13
2	Tensile strength	210	246	248
	Elongation	745	742	736
	Modulus at 400%	26.4	31.0	32
	Tear-resistance	4.83	5.20	6.30
5	Tensile strength	216	292	293
	Elongation	725	705	687
	Modulus at 400%	33.3	43.3	53.2
	Tear-resistance	4.25	5.20	9.30
10	Tensile strength	226	312	325
	Elongation	676	682	670
	Modulus at 400%	46.3	67.5	90
	Tear-resistance	3.30	5.34	1.37

TABLE IX

MECHANICAL PROPERTIES OF A SERIES OF MIXES CONTAINING A STANDARD QUANTITY (10 VOLUMES) OF INDIVIDUAL FILLERS AND THEIR MIXTURES. CURE AT 125.5° C. OPTIMUM VULCANIZATION

Base mix: same as in Table VIII

Volumes of carbon black....	0	2.5	5	7.5	10
Volumes of clay.....	10	7.5	5	2.5	0
Tensile strength.....	226	280	312	314	325
Elongation at break.....	676	683	682	684	670
Modulus at 400% elongation	46.3	58.2	67.0	76.5	90.4
Tear-resistance, kg. per cm...	3.30	4.05	5.30	9.50	14.30

The present investigation has confirmed the opinion that tear-resistance in vulcanized rubber is intimately associated with the interfacial relationships between the rubber and filler particles. Work is now in progress with a view to modifying the surface characteristics of fillers in order to increase their adhesion to the rubber phase of vulcanized compounds and hence improve tear-resistance.

Summary

1. The importance of tear-resistance as a criterion of the interfacial relationship between rubber and its fillers has been emphasized.

2. Existing methods of determining resistance to tear in vulcanized rubber have been described, and subjected to a critical examination.

3. The disadvantages peculiar to each of the above methods have been discussed, and experiments whereby it was aimed to overcome these sources of errors are described.

4. A new method of determining resistance to tear has been evolved, whereby the tearability is measured in terms of the mean of the initial and final loads required to tear a 4-mm. length of a butt-ended test-piece prepared by punching with a standard dumb-bell die from the inner disc of a 6-mm. ring test-piece. Figures are given to indicate the consistency of the results.

5. Experimental data obtained by different tear methods are discussed in relation to those measured with the new butt-ended test-piece; and reasons for wide divergence between the numerical results explained.

6. The effect of calender grain (mechanical anisotropy) on the tear-resistance of vulcanized rubber has been investigated and it was found impossible in many cases to effect tearing across the grain. Hence, measurement on non-grained test-pieces has been adopted.

7. A new manner of presenting tear-test results is proposed whereby the deformation of the test-piece is taken into account by direct measurement of the width of the tearing plane. Such a method takes cognizance of the unquestioned influence of modulus in rubbers of different compositions.

8. The resistance to tear of rubber compounded with refined china clay has been investigated. Such a clay results in a lowering of the tear-resistance of vulcanized rubber, but it has been found possible to improve this aspect by control of the vulcanizing conditions. Accelerators active at low temperatures were shown to be capable of producing a vulcanized product of exceptional tear-resistance.

9. The effects of mixtures of china clay and carbon black were compared with those of the two fillers separately, and it was found that the tear-resistance of rubber compounded with mixtures was below that anticipated from the algebraic sum of the effects of the same amount of the components separately.

The authors wish to record their thanks to Dr. Drakeley for the help and advice given during the course of this investigation.

One (G. L.) of the authors is indebted to the Ramsay Memorial Fellowship Trust and the University of Athens for the award of a Fellowship which permitted him to undertake this investigation in England.

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The Abrasion Question

Some Factors in the Deterioration of Rubber When Exposed to Frictional Contacts with Other Materials

V. A. Cosler

Any discussion of the factors entering into the wearing away of rubber compositions when exposed to frictional contacts with other materials rapidly becomes complicated by the introduction of the word "abrasion." An analysis of the conditions existing when rubber is disintegrated by frictional relation with other materials will disclose the fact that these conditions are caused by a number of different fundamental reactions taking place at the same time.

It therefore follows that a rubber composition, which resists any given set of disintegrating conditions, must have characteristics which enable it to resist each of these reactions to a different degree. Sometimes it is necessary to balance these properties and sacrifice some in order to emphasize others which are more important in that particular set of disintegrating conditions. It is this need for balancing one characteristic of a rubber composition against another which makes it advisable to consider from a broad point of view the whole proposition of testing rubber compositions for their resistance to disintegration when in frictional relation with other materials.

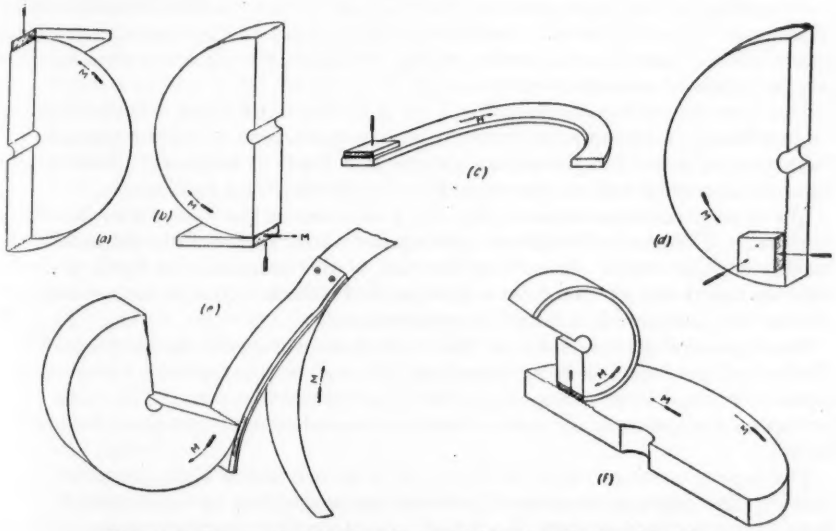

Figure 1—Diagrams of Various Types of Abrasion Testing Machines

The rubber industry has displayed a keen interest in the reactions which take place when rubber is exposed to such contacts, but owing to the fact that the pneumatic tire dominates the interests of the industry, these reactions have been studied largely from the point of view of resisting the peculiar and particular combination of conditions which are present as a tire tread is worn away by contact with a road surface.

The tests tending to evaluate a rubber composition under this particular set of frictional conditions have come to be called, generally, abrasion tests. Before further discussion as to the probable value of recognized abrasion tests when applied to the general problem of studying all the factors which enter into the many different kinds of actual service conditions, it will be necessary to study these well-known and generally used abrasion testers. Figures 1 and 2 show by simple diagrams the principles involved in most of the testers at present on the market. There has been no attempt made to describe the mechanism which holds the rubber specimen in contact with the abrasive material, since such information is available in profusion. The purpose of this paper is not to discuss the relative merits or demerits of the various machines in regard to their ability to give duplicate results, but rather to discuss their ability to duplicate the results obtained by different sets of actual service conditions.

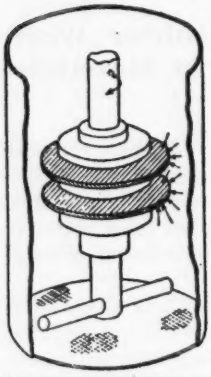

Figure 2—Sproul-Evans Abrasion Tester

In these diagrams, arrows designated *M* represent forces which produce movement. Arrows not so designated represent known and balanced forces. The rubber specimen is indicated by that portion of the drawing which is shaded. The abrasive surface is represented by a series of notches.

The type of machine shown in Fig. 1 (*a*) is best exemplified by the Sigler-Holt[1] or Bureau of Standards machine. Results are given as volume of material removed in a given period of time compared to that removed from a standard or known test-specimen. There are several machines of this type, but they are all upon the general idea of a stationary block of rubber held against a revolving abrasive surface by means of a known weight.

The type of machine shown in Fig. 1 (*b*) is known as the United States Rubber Co. machine,[2] and follows the principle of exposing a moving rubber specimen to the action of a revolving abrading surface at a point of tangency. Results are reported as volume-loss compared to that of a standard test-specimen.

The type of machine shown in Fig. 1 (*c*) is known as the New Jersey Zinc Co. machine.[3] The block of rubber is held against an abrasive surface attached to a moving circular track. In one modification of this machine, the block is alternatively raised and lowered from contact with the track. Results are reported as volume-loss compared to a standard test-specimen.

The type of machine shown in Fig. 1 (*d*) is known as the du Pont abrader.[4] The rubber specimen is held by a constant force against the flat side of a revolving abrasive wheel. Results may be recorded as volume-loss per unit of work performed on the specimen, or units of work performed to remove a given volume of rubber.

The type of machine shown in Fig. 1 (*e*) is known as the Kelley abrasion machine.[5] The diagram shows one of the specimens attached by means of a flexible metallic clip to the periphery of a wheel. As the rubber specimen passes a point between the above-mentioned wheel and an oppositely revolving abrasive wheel, it is forced into contact with the periphery of the latter. The results are reported as volume-loss compared to that of a standard sample attached to the same wheel by the same means.

The type of tester shown in Fig. 1 (*f*) is exemplified by the Dunlop machine,[6] and by the machine described by Tronson and Carpenter[7] as the Vogt-Goodyear machine.[8] The Bureau of Standards also used a machine[8] involving this same

general principle, that is, a rubber specimen contacting with an abrasive surface both of which have a revolving motion. This type of machine is operated with known relations between the peripheral speed of the specimen-bearing wheel and the abrasive-bearing wheel. The specimen-bearing wheel may drive the abrasive-bearing wheel in the same manner as a friction clutch, or the abrasive wheel may drive the specimen wheel, or both may be driven. The results are reported as comparative volume-loss between testing specimen and a standard.

The apparatus used in the Sproul-Evans abrasion tester[9] is shown in Fig. 2. The specimen is completely immersed in a uniform-sized abrasive such as carborundum particles. The specimen-bearing shaft revolves in the loose abrasive. The bottom of the cylinder is a sieve and as the carborundum particles are reduced in size, due to the grinding against the specimen and shaft, they are automatically sieved out. The small arrows in the diagram represent the impingement of these carborundum particles against the rubber specimen. The results are reported as volume-loss of material compared to that of a standard sample held in relatively the same position and exposed to the same conditions of abrasive wear.

It will be noted that there is a similarity of conditions in all types of testers represented by the diagrams in Fig. 1. With a definite purpose in mind the abrasive surfaces of these various types of testers have been indicated by serrated edges. If a section be taken through that part of the device which carries the abrasive surface, any such section can be visualized as a thin paddle with a serrated or jagged edge.

Analysis of the motion which is produced by the machines will disclose the fact that the six types operate on the fundamental principle of dragging a paddle with a serrated edge over the surface of the rubber specimen. One machine drags the paddle straight across, others through an arc, some with more force at one point than at another, but all fundamentally perform the same operation, that is, drag the serrated edge across the surface of the sample or the sample across the serrated edge of the paddle, or both.

In the case of the Sproul-Evans type, however, it is necessary to visualize the action from a little different point of view. In this case it is necessary to assume a saw-toothed paddle with no strength in a direction normal to the specimen being tested. In other words, the serrations have been removed from the paddle and placed in a cylinder, so that they impinge only by their own weight against the rubber specimen which is revolved in relation to the sides of the cylinder. The difference in the results obtained by the use of this machine, compared to the other six types, becomes important in the discussion which will follow later.

Having considered the principles involved in abrasion testers, let us consider various service conditions existing as rubber is exposed to frictional relations with other materials in commercial practice. Some of the commercial products which operate under service conditions where deterioration is caused by frictional relations with other materials are:

1. Pneumatic tire treads.
2. Conveyor belt covers (conveying materials ranging from mail packages to hot coke).
3. Chute linings.
4. Ball and rod mill linings.
5. Rubber heels.
6. Floor coverings.
7. Dredging sleeve tubes.
8. Covers of many kinds of hose.
9. Sand-blast hose tubes.

These are only a few of the commercial applications, but it will be advisable to consider these applications in order to give point to the discussion which follows.

It is obvious that in order to evaluate a rubber composition to be used in any one of these articles, it will be necessary to evaluate the composition as to a number of qualities possessed by it.

The characteristics which have been suggested as of probable importance are:

1. Resistance to cutting.
2. Resistance to tearing.
3. Resilience (ability to cause rebound).
4. Stress-strain relations.
5. Changes produced in any of the above by:

(*a*) Aging,
(*b*) Heat,
(*c*) Exposure to light, or
(*d*) Conditions of stretch or distortion.

These suggested characteristics have been discussed in connection with the work done on abrasion testing by the Society's Committee D-11 on Rubber Products[10] and more recently and fully in a paper by H. A. Depew.[11]

It is not to be assumed that the above-mentioned properties are the only ones which should be evaluated, nor can it be assumed that each one named is fundamental; however, the list is complete enough to give a general idea of the properties which are important in evaluating a rubber composition as to its ability to withstand a given set of deteriorating influences. It is obvious that each of these factors is of more importance under one set of circumstances than under another. To illustrate this point, let us consider the characteristic of resistance to cutting. We can arrange the products mentioned above in an order which represents roughly the relative importance of this characteristic under the conditions of service of that product. That is to say, resistance to cutting is more important in the first product in the following list than it is in the second or third, etc. The order of importance indicated below is a matter of personal judgment and is based on observation only:

1. Conveyor belt covers.
2. Pneumatic tire treads.
3. Heels.
4. Floor coverings.
5. Hose covers.
6. Dredging sleeve tubes.
7. Ball and rod mill linings.
8. Chute linings.
9. Sand-blast hose tubes.

However, if we were to consider the need for a high degree of resilience (ability to rebound), the author would arrange the articles in a different order of importance, as follows:

1. Sand-blast hose tubes.
2. Chute linings.
3. Ball and rod mill linings.
4. Conveyor belt covers.
5. Pneumatic tire treads.
6. Hose covers.
7. Dredging sleeve tubes.

8. Heels.
9. Floor coverings.

These two different arrangements serve to emphasize the fact that every set of service conditions requires a different type of compound with a different balance of characteristics.

A concrete example is available in the tube of sand-blast hose. A good sand-blast hose tube will not make a good tire tread, nor will a good tire tread make a good sand-blast hose tube. While a good sand-blast hose tube will not necessarily be entirely lacking in resistance to cutting, nevertheless its most outstanding property will be a high degree of resilience. Since compositions which have a high resistance to cutting are, generally speaking, reinforced to such a degree as to lower their resilience somewhat, it will be necessary to sacrifice some of this resistance to cutting in order to emphasize and increase the resilience of the composition. Thus the compound is balanced to meet the demands made on it by service conditions.

Now, let us reconsider abrasion testers from the point of view of duplicating the actual condition of service requirements. It is obvious that in order to simulate any given set of service conditions, it will be necessary to vary the conditions obtaining between the specimen and the abrasive in the testing device to the same degree and in the same proportions as is the case between one set of actual wearing conditions and another.

No evidence has been collected which indicates the possibility of making such adjustments in machines now being used. In fact, there is, by inference, evidence which denies the possibility of producing such variations.

It has been established that the Sproul-Evans type of abrasion tester will produce results indicating that a good sand-blast hose tube compound has a higher resistance to abrasion than a proved tire tread, but in spite of repeated attempts, no change in operating conditions of the machine could reverse this order of evaluation.

As far as the author has been able to discover, no change in the operating conditions of the other six types of machines will show a tire tread inferior to a sand-blast hose tube. It is true that the operators have been almost invariably trying to check evaluation figures against tire tread compounds of known relations rather than to reproduce sand-blast conditions, but nevertheless the principles involved in the construction of the machines represented by Fig. 1 militate against duplicating conditions corresponding to this service, just as the construction of the Sproul-Evans machine (Fig. 2) prevents it duplicating tire road conditions.

Another example which has a bearing on the discussion at this point is a series of tests run in connection with an attempt to evaluate heel compounds. Two types of abrasion testers produced results which indicated that a good tire tread compound was superior to a good heel compound in abrasion resistance. Walking tests under severe conditions confirmed these results, but when two different types of heel compounds were tested on one machine the results obtained in walking tests were reversed, that is, the compound which gave best results in the laboratory was inferior when applied to shoes and tested. Results obtained on another machine gave the compounds proper positions with respect to one another when compared to walking tests, but the magnitude of difference was not comparable with results obtained in service. The results of walking tests are visual so that the data cannot be presented, but almost any manufacturer of mechanical rubber goods has had similar experiences on products, which owing to material-cost necessities vary from tire treads and from one another in several physical properties.

Summary

If we accept the proposal that the fundamental effect produced by the machines diagrammed in Fig. 1 is that of dragging a series of saw-toothed paddles across the surface of rubber specimens, we must accept as fact the theorem that the results recorded by these types of machines is a summarization of values rather than a fundamental value.

If we accept the evidence that relations cannot be varied on any type of present abrasion testers to duplicate the conditions existing in all situations where rubber is exposed to frictional contacts with other materials, we must accept the fact that some fundamental factor is absent, or is over- or under-emphasized as these relations are varied.

Whether these missing reactions can be supplied by evaluating other characteristics which will properly modify the results obtained on any given abrasion tester is an open question.

It can be safely stated, however, that results obtained from any type of tester discussed can only be considered as evaluating rubber compositions at or near the point of optimum cure under one particular set of wear conditions. With one exception these conditions may safely be considered as approximating the conditions obtaining between a tire tread and the road under normal operating conditions.

The Sproul-Evans tester may safely be considered as more closely approximating sand-blast hose conditions than tire-road conditions.

It is the thought of the author that the most promising field of future endeavor lies in the direction of studying the possibility of reproducing more fundamental effects, rather than attempting to add more reactions to the already complex set of conditions present in the known types of abrasion testers.

The suggestion is also offered that a most promising field of study lies in the direction of studying the modifying effect of distortion upon the fundamental characteristics of rubber, and attempting to establish the extent of distortion present when rubber is exposed to frictional disintegration in actual service conditions.

[1] Sigler and Holt, "A Simple Abrasion Test Machine for Rubber," *India-Rubber World*, **82**, No. 5, 63 (1930).

[2] Henry L. Scott Co., Providence, R. I.

[3] Depew, "An Explanation of Some of the Difficulties in Abrasion Testing of Rubber," *Proc. Am. Soc. Testing Materials*, **28**, Part II, 871 (1928).

[4] Williams, *Ind. Eng. Chem.*, **19**, 764 (1927).

[5] Hardman, MacKinnon, and Jones, *Rubber Age*, **28**, 463 (1931).

[6] Lambourn, *Trans. Inst. Rubber Industry*, **4**, 210 (1928).

[7] Tronson and Carpenter, "Abrasion Tests of Vulcanized Rubber Compounds Using an Angle Abrasion Machine," *Proc. Am. Soc. Testing Materials*, **31**, Part II, 908 (1931).

[8] Holt and Wormeley, U. S. Bureau of Standards, *Technologic Paper* **294** (1928).

[9] Evans, "An Apparatus and Method for Determination of Resistance to Abrasion of Rubber Products," *Proc. Am. Soc. Testing Materials*, **23**, Part II, 517 (1923).

[10] Symposium on Abrasion Testing of Rubber, *Ibid.*, **31**, Part II, 895 (1931).

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Research Paper No. 544.]

The Preparation and Crystallization of Pure Ether-Soluble Rubber Hydrocarbon: Composition, Melting Point, and Optical Properties

W. H. Smith, Charles Proffer Saylor, and Henry J. Wing

I. Introduction*

Substantially all of the chemical and physical evidence concerning the nature of rubber is consistent with the chemical formula $(C_5H_8)_x$, and this is the generally accepted formula for "rubber hydrocarbon." An examination of the evidence discloses, however, that the above formula is not the only one which is consistent with this evidence. The difficulty of establishing beyond question the chemical composition of rubber hydrocarbon has been due largely to the lack of efficient physical methods for fractionating the hydrocarbon, of proving that the final fractions are one-component systems, and of chemically identifying these fractions. If, as seems not improbable, rubber hydrocarbon is a mixture of closely related hydrocarbons not all of which can be represented by the formula $(C_5H_8)_x$, no single method of fractionation can be relied upon to separate this mixture into its constituents. The only methods heretofore available for this purpose have been those based upon extraction with different liquids and fractional precipitation. One of the most powerful methods for fractionating a mixture of hydrocarbons is systematic crystallization, and the purpose of this investigation was to develop a technic for applying this method to rubber.

II. Purification and Crystallization of Rubber Hydrocarbon

W. H. Smith

1. Purification

Rubber hydrocarbon readily undergoes changes in structure of an unknown character. Light, for example, changes the viscosity of rubber solutions, and the addition of a small amount of mineral acid rapidly decreases it. Crude rubber which is used in the preparation of commercial rubber cements must be masticated before it is dissolved in organic solvents or solution may be incomplete. Busse[1] has shown that the mastication of rubber requires oxygen to produce plasticity. Pure rubber hydrocarbon quickly oxidizes when exposed to air. The natural oxidation inhibitors of *Hevea* rubber, two sterol-like compounds, have been isolated by Bruson, Sebrell, and Vogt.[2]

Rubber of commerce, which is obtained chiefly from the latex of *Hevea brasiliensis*, contains various other substances in addition to rubber hydrocarbon. These nonrubber materials may be classified as water-soluble, acetone-soluble, protein or

* The introduction is part of a note by Washburn, *Phys. Rev.*, **38**, 1790–1791 (1931).

other nitrogenous compounds, and mineral substances. Reviews of existing methods for preparing pure rubber hydrocarbon are given by Pummerer and Koch,[3] and by Pummerer and Miedel.[4]

Some form of commercial coagulated rubber was the raw material formerly used in attempts to prepare pure rubber hydrocarbon. Pummerer and Pahl,[5] however, used latex, which is preferable to coagulated rubber because the impurities are readily attacked in an alkaline dispersion. In their method, the latex is treated three or more times at 50° C. with a 2 per cent solution of sodium hydroxide to remove protein. After each treatment, the rubber particles coalesce or "cream" in an upper layer, and the impurities in the lower layers are drawn off. At the conclusion of the third treatment, neither the biuret reaction nor the ninhydrin reaction shows the presence of nitrogen in the rubber hydrocarbon. The alkali is finally separated by dialysis. The solutions are saturated with nitrogen during purification to protect the rubber from oxidation.

The use of trypsin to remove protein qualitatively from rubber in latex was first tried by Spence.[6] Later Freundlich and Hauser[7] used it to remove protein in *Hevea* latex and observed microscopically the disappearance of protein adsorbed on the rubber particles.

Rubber may be separated into two fractions by ethyl ether. Petroleum ether has also been suggested for the purpose by Caspari.[8] The fractions are called, in the literature, alpha and beta, or sol and gel phases. Ethyl ether has been used in the present work, and throughout this paper the fractions are called, respectively, the ether-soluble and ether-insoluble portions of the total rubber hydrocarbon.

When crude rubber of commerce is extracted with ether, the soluble rubber is quite pure, as Feuchter[9] has indicated, and the impurities are concentrated in the insoluble portion.

According to Pummerer,[10] from 65 to 75 per cent of the total rubber is soluble in ether, and Bruson, Sebrell, and Calvert[11] reported that 75 per cent of the material was ether-soluble. They noted also that the "polymers" of rubber formed by treating it with tin tetrachloride could be separated by benzene, and that the ratio of soluble to insoluble "polymer" was 75 to 25. Whitby[12] believes that "the coincidence of these proportions was probably fortuitous." He has noted the wide variation reported in the literature on the relative amounts of soluble and insoluble rubber. The work of the Midgley Foundation[13] on the fractional precipitation of rubber indicated that unmilled pale crepe contains a single "sol" component, which amounts to more than one-half of the material.

Pummerer and Koch[14] were the first investigators to report the isolation of crystalline rubber. More recently, however, Pummerer and von Susich[15] have stated that the crystallized material reported by Pummerer and Koch was not rubber but alpha gutta-percha.

In the course of work on the purification of rubber hydrocarbon by the author, several lots of pure material were prepared by the method of Pummerer and Pahl. It was observed that the treatment of latex with a 2 per cent solution of sodium hydroxide at 50° C. causes the ether-insoluble fraction to become partly soluble. At 60° C. the effect is intensified. At 80° C., however, much of the ether-soluble fraction becomes insoluble. This behavior was subsequently confirmed on isolated ether-soluble and insoluble hydrocarbon. Therefore, to separate the two fractions, it is necessary that contact with alkali at 50° C. be avoided, if a partial conversion of the ether-insoluble fraction into an ether-soluble form is to be prevented.

It appeared possible to use trypsin for the quantitative removal of protein.

The enzyme mixture in technical preparations of trypsin is effective between p_H 8.2 and p_H 10.2. A 3 per cent aqueous solution of sodium bicarbonate provides a suitable medium, and a temperature of 38° to 39° C. is satisfactory. It was observed that if digestion of the protein in the latex takes place in the presence of a 3 per cent solution of sodium bicarbonate, the subsequent addition of sodium hydroxide equivalent to a 2 per cent solution causes creaming at room temperature. Under these conditions, the sodium hydroxide solution is used only as a creaming agent at room temperature, in accordance with DeVries and Beumée-Nieuwland's[16] technic, and the action of alkali on latex at 50° C. is avoided.

With the above observations as a basis, a method of purification was developed in which it was sought to maintain unchanged the structure of rubber hydrocarbon, and also to permit a sharp separation of the ether-soluble and insoluble fractions. Throughout the purification, until the coagulated rubber was extracted with acetone, the rubber hydrocarbon was protected against the action of light, which produces a gel in an ether solution of the hydrocarbon. It was also protected against the action of oxygen by the natural antioxidants, which have a powerful protective action. The antioxidants were extracted from commercial smoked sheet according to the method of Bruson, Sebrell, and Vogt.[17] An amount sufficient to keep the rubber protected was added to the latex at intervals and later removed from the coagulated rubber by extraction with acetone. The antioxidants were not isolated, but were used in concentrated alcoholic solution after freezing out phytosterol and octadecyl alcohol. The alcoholic solution of antioxidants was kept under nitrogen to preserve their protective action.

The details of the method of purification are as follows: Four hundred milliliters of 38 per cent commercial ammoniated latex were dialyzed, using a bag of washed cellophane. According to the observation of Beadle and Stevens,[18] from 20 to 25 per cent of the total nitrogen derivatives is dialyzable, and they are consequently removed with the ammonia. Dialysis was continued until the latex was almost free from ammonia. At its conclusion, the latex, already considerably diluted, was further diluted with distilled water to a volume of 2500 ml. About 80 g. of sodium bicarbonate were added to make approximately a 3 per cent solution. The latex was warmed to 38° C. in an oven, after which a filtered aqueous solution of trypsin containing about 2.0 g. was added. If the trypsin is added at room temperature, coagulation may occur. The mixture was maintained at 38° C. for 10 hours, and afterward was allowed to cool to room temperature. A solution of sodium hydroxide was added to produce a concentration of 2 per cent. Creaming commenced immediately and after one or two hours the lower layer, containing the impurities but practically free from rubber, was removed. Another portion of 2 per cent sodium hydroxide solution was added and creaming was repeated with subsequent removal of the lower layer. The number of creamings necessary to reduce the impurities to a negligible amount was estimated from the relative volumes of the upper and lower layers, by assuming that the soluble impurities were uniformly distributed between the layers at each washing. After the final washing the creamed rubber was dialyzed through a washed cellophane membrane until neutral to phenolphthalein. A portion of the rubber coagulated as the last traces of alkali were removed. The remainder was in some cases coagulated by adding acetone and passing a brisk current of nitrogen into the mixture to cause collision and adhesion of the rubber particles. In other cases the rubber was obtained by electrodeposition. The coagulated or electrodeposited rubber, still containing added antioxidant, was cut into strips and dried *in vacuo* at room temperature. It was then cut into small pieces (2 cu. mm.), extracted with acetone for 20 hours, and dried in a vacuum. The product was transparent and amber-

colored. The amount of nitrogen in the purified total rubber before extraction with acetone was found to vary between 0.008 and 0.02 per cent, determined by the Kjeldahl method. The extracted rubber was free from nitrogen when analyzed by the same method.

The total rubber which had been extracted with acetone was subsequently extracted with ether. This operation was performed at times in a Soxhlet extractor and at other times in the apparatus suggested by Pummerer, Andriessen, and Gündel.[19] In each instance a stream of nitrogen was passed through the ether during extraction. In the course of the work it was observed that when rubber is protected by the natural antioxidant during purification, approximately 75 per cent of the total rubber is soluble in ether. The solution of rubber hydrocarbon, suitably diluted with ether, and saturated with nitrogen, was used to obtain crystalline rubber hydrocarbon. These crystallizations were not confined to one lot of material but represent rubber hydrocarbon which was purified at intervals from different shipments of ammoniated latex.

2. Crystallization

The conditions necessary for the formation and growth of crystalline particles have been formulated by Tammann,[20] by von Weimarn,[21] and by others. Purity is necessary, particularly freedom from material which might be adsorbed on the crystal nuclei. With rubber this means freedom from material of a nitrogenous nature. The fluidity should be high enough to provide sufficient mobility for the formation of nuclei, and the solution should be dilute in order to keep the number of nuclei at a minimum. The temperature should be sufficiently low to start the formation of nuclei and to provide a suitable medium for their continued growth.

Solutions of different concentrations of ether-soluble rubber, dissolved in anhydrous ether, were prepared and subjected to successively lower temperatures, beginning at −10° C. At −65° C., with a concentration of 1 part of rubber to 2000 parts of ether, tiny particles of material which were birefringent under crossed nicols separated after about one hour. The particles grew slowly and formed aggregates. These developed into larger aggregates during a period of several hours, and after about 12 hours the entire mass settled as a clot. Repeated experiments confirmed the observations. Concentrations of 1 part of rubber in 2500, 3000, and 3500 parts of solvent gave similar results, but with increasing slowness.

The velocity of formation of nuclei under such conditions is high, and crystal habit is not established. Crystal habit is developed by using Tammann's[22] procedure, which permits the formation of only a few nuclei, and these are subsequently grown under conditions such that the formation of new nuclei is at a minimum and the velocity of crystallization is suitable.

Two Dewar flasks were used, one a silvered half-liter flask and the other of 4 liters capacity. The smaller flask was supported in the larger flask, which was inclosed in several layers of insulating felt. Each flask contained acetone at −58° C. A tube containing the ethereal solution of the rubber hydrocarbon was cooled to −65° C. for 15 minutes and then allowed to warm to −58° C., at which temperature it was immersed in the acetone contained in the smaller Dewar flask. During a 24-hour interval the temperature increased about 15°. Although the temperature rose, the velocity of crystallization was low and a satisfactory degree of supersaturation was maintained. The rubber deposited on the sides of the tube in small nodules which appeared to have developed radially from a point in the center. By maintaining suitable conditions for a longer period, nodules half a millimeter in diameter or larger are produced. Approximately 95 per cent of the rubber crys-

tallizes at −65° when the initial concentration is 1 part of rubber in 2500 parts of ether.

Material prepared as nodules was used in the examination of optical properties and in the determination of the hydrogen-carbon ratio.

In addition to the crystals of ether-soluble rubber obtained as described above, crystals of the ether-insoluble form of rubber have also been produced. These latter crystals differ materially from the ether-soluble crystals both in appearance and in melting behavior. They will be discussed in a later paper.

IV. Microscopical Study of Crystalline Rubber

Charles Proffer Saylor

The low temperature which is necessary for the nodules of rubber hydrocarbon to be stable in contact with their ether solution makes it impossible to watch their

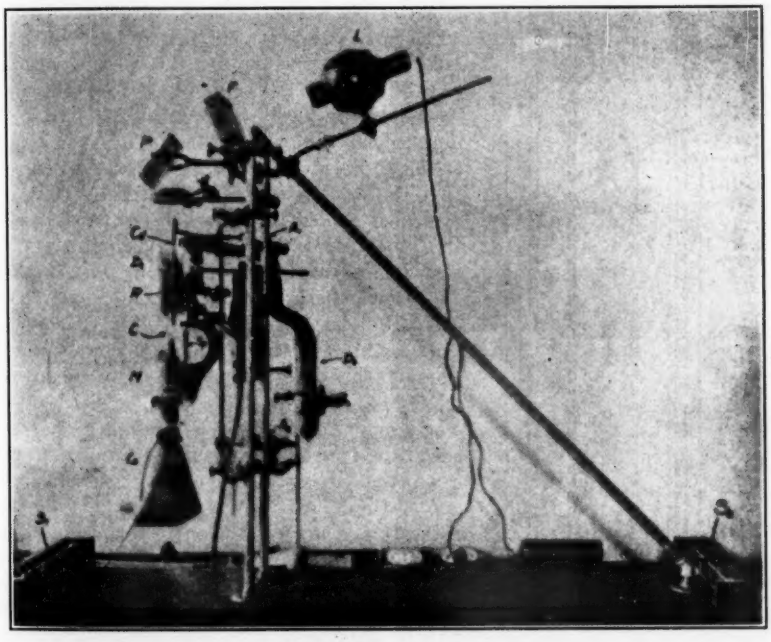

Figure 1—Assembly of Apparatus

C, cell; D_1, Dewar flask with optically plane windows at bottom; *Cd*, optical condenser; *L*, projection lamp; *F*, light and heat filter; *P*, polarising reflector; *M*, microscope; *Ca*, camera; D_2, Dewar flask to contain liquid air; *R*, refrigeration coil; *A*, A_2, axis of rotation for D_1, *Cd*, *R*, and *C*; *Sp*, spring to overcome weight of microscope tube; S_1, S_2, spring suspension.

growth or determine their properties by the usual microscopical methods. Several forms of apparatus[23] have been used in the examination of crystals at low temperatures, but, since none of them was entirely suited to the uses described in this paper, an apparatus was designed by means of which the crystallinity of the nodules was established and some properties of the crystals were determined.

1. The Apparatus

The apparatus which was employed is illustrated in Fig. 1. It departs from that commonly used in photomicrography between crossed nicols chiefly in three par-

ticulars: (1) The sample is contained in an unusual form of cell; (2) a Dewar flask with optically plane windows at the bottom holds the cell and its temperature bath; and (3) a long range immersion condenser, capable of focusing the light source on the crystals at the bottom of the cell, is employed. The details of these parts are represented in Fig. 2. The cell and Dewar are made entirely of Pyrex glass. The cell is a cylinder with an inside diameter of 12 mm. and a height of 10 mm. To its polished upper and lower edges are sealed the ground and polished disks, 0.5 mm. thick, which serve as windows. Two tubes for filling and emptying connect with the cylinder. One of them is bent downward inside the cell and nearly touches the surface of the bottom disk. The windows of the Dewar flask, which also are polished, optically plane disks of glass sealed to polished edges on the flask, are 1 mm. thick, 30 and 24 mm., respectively, in diameter, and 1 mm. apart. When the cell rests on the inner window of the Dewar flask, the distance from the crystals on its bottom to the outside of the flask is 3.5 mm. Therefore, though the crystals were viewed at temperatures as low as −90° C., it was possible to use a 16 mm. objective, N. A. 0.25. An excessive amount of glass intervened between the objective and its focal plane, but satisfactory images were formed despite this handicap. The Dewar flask contained acetone, which was cooled by drawing liquid air from flask, D_2 in Fig. 1, through the coil, R, of copper tubing. Temperatures were determined by means of a triple junction, copper-constantan thermocouple. The condenser, Cd, was so designed that it focused the entire beam from the projection lamp upon the preparation, forming an image the size of the microscope field. The microscope, a petrographic model with a rotating tube analyzer, was bolted by its base to the vertical support. A rotation of 90° at the pillar joint permitted complete inversion of the instrument. Except when refractive indices were determined, a multiple plate polarizer served as the primary nicol. A tube camera with side telescope was used both for viewing and for photographing preparations in the cell. The positions of the Dewar flask, the condenser, and the coils of copper tubing were adjusted on a swinging support so that they were coaxial with the microscope when the support was pushed against stops and clamped.

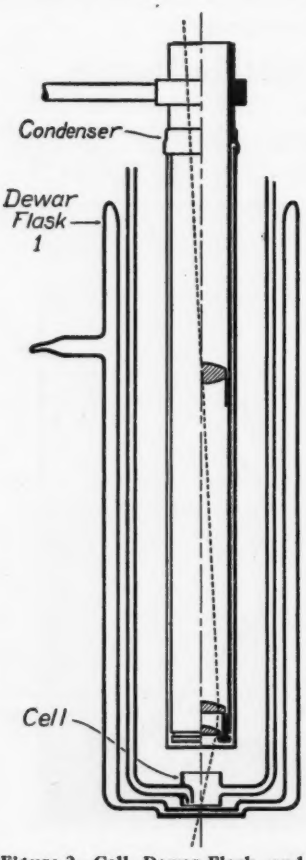

Figure 2—Cell, Dewar Flask, and Condenser

The dotted line indicates the course of a beam of light. It intersects the center line at levels where images of the arc crater are formed.

2. The Crystals of Ether-Soluble Rubber Hydrocarbon

A solution of ether-soluble rubber hydrocarbon was treated as has been described. This treatment caused the formation of nodules on all walls of the cell. More nodules formed on the bottom of the cell, however, than on any of the other surfaces. If the cell was removed from the bath, the upper surface touched briefly

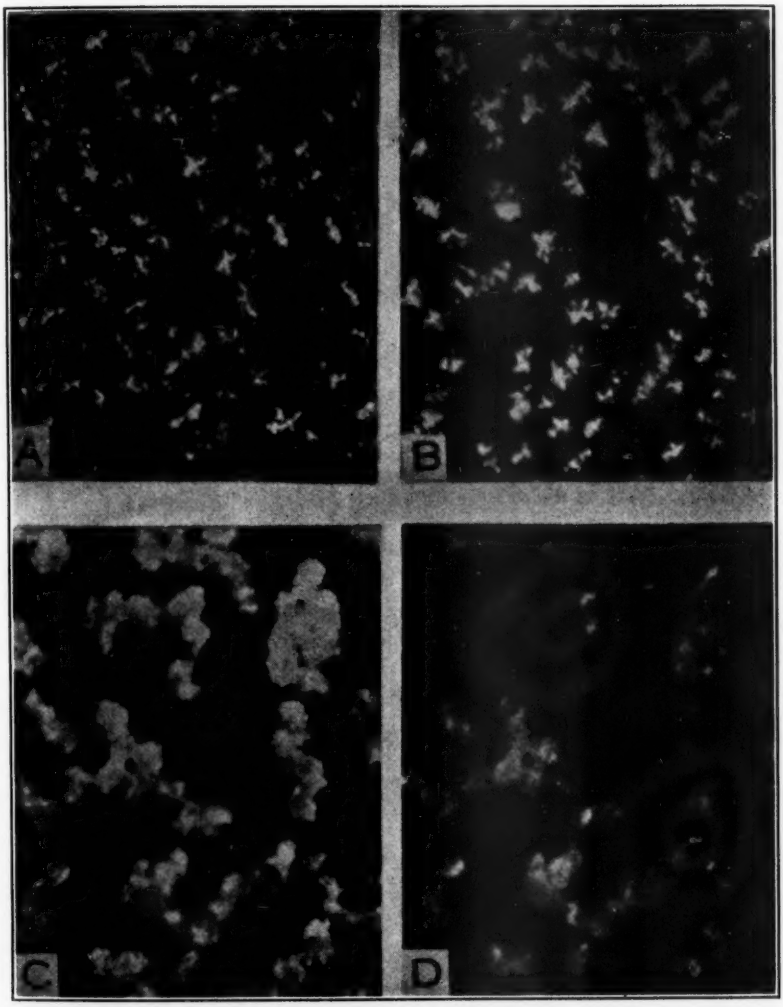

Figure 3—Photomicrographs Showing Melting of Ether-Soluble Hydrocarbon Crystals

A, crossed nicols. ×200. Rubber crystals surrounded by mother liquor. They are roughly spherular clusters of birefringent crystals. The brightness of the clusters is created by their optical anisotropy. Temperature, −50° C. Exposure, 1 second.

B, crossed nicols. ×200. A similar field after the mother liquor has been withdrawn. Otherwise, except for optical distortion produced by the adhering liquid, there is no significant difference. The different clusters can be seen in the same position in this and succeeding photomicrographs. Temperature, −45° C. Exposure, 5 seconds.

C, crossed nicols. ×200. Same field as *B*. The ether has all been evaporated by suction. Surface tension has distorted the crystals. As a consequence the brightness of birefringence is less. This is indicated by the greater exposure. Temperature, −40° C. Exposure, 12 seconds.

D, crossed nicols. ×200. Same field as *B*. Just below the melting point. The principal difference between this and *C* arises from differences in the photomicrography. Temperature, +8.4° C. Exposure, 12 seconds.

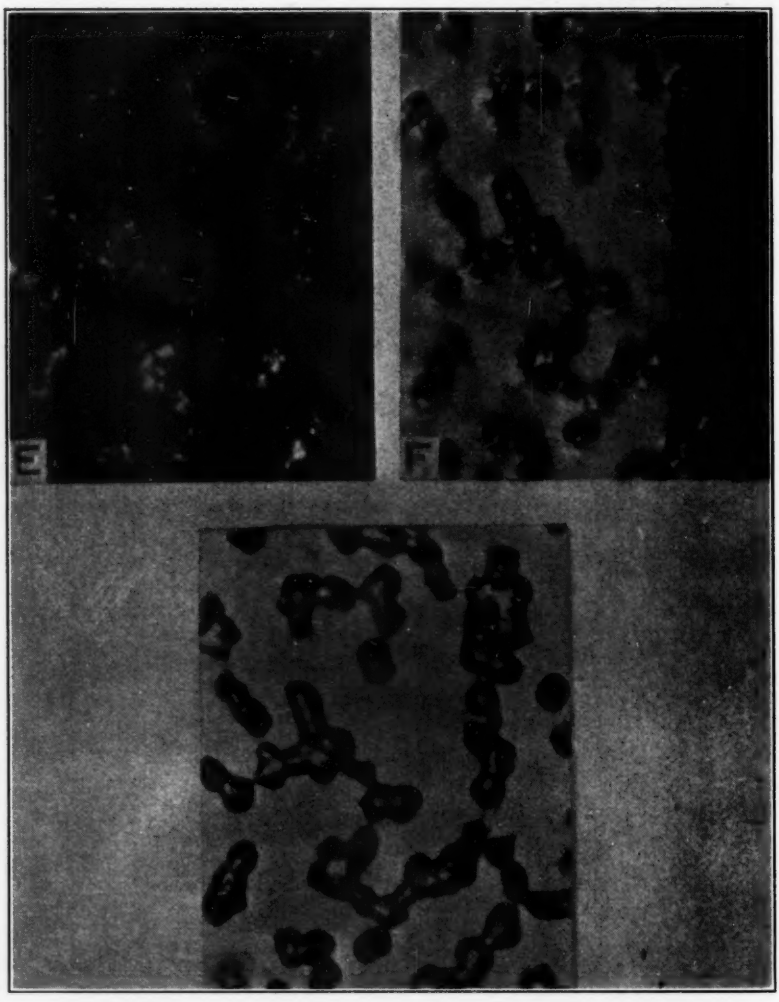

Figure 3 (Continued)—Photomicrographs Showing Melting of Ether-Soluble Hydrocarbon Crystals

E, crossed nicols. ×200. Same field as *B*. Much of the birefringence has disappeared. It is supposed that the more severely distorted crystals have melted below the true melting point. Those which are less distorted persist unchanged. Temperature, +9.7° C. Exposure, 12 seconds.

F, crossed nicols. ×200. Same field as *B*. Very long exposure so that extinct field appears bright. Birefringence has disappeared. Groups are beginning to flow into globules. Temperature, +11.8° C. Exposure, 1 minute.

G, parallel nicols. ×200. Same field as *B*. Because of the smallness of the clusters, the surface tension forces have been relatively large. Melted ether-soluble rubber hydrocarbon has flowed into rounded globules. Temperature, +12.6° C. Exposure, 1/10 second.

with a finger, and the cell replaced in the bath, the temporary warmth caused the crystals at the spot touched to dissolve but did not disturb those on the bottom of the cell. The alcohol in the Dewar flask was cooled to −50° C. The cell was transferred to the flask, and the revolving carriage which supports the Dewar flask, cooling coil, condenser, and cell was swung into the optical axis of the microscope. Viewed between crossed nicols, the crystals appear as in Fig. 4.[24] They

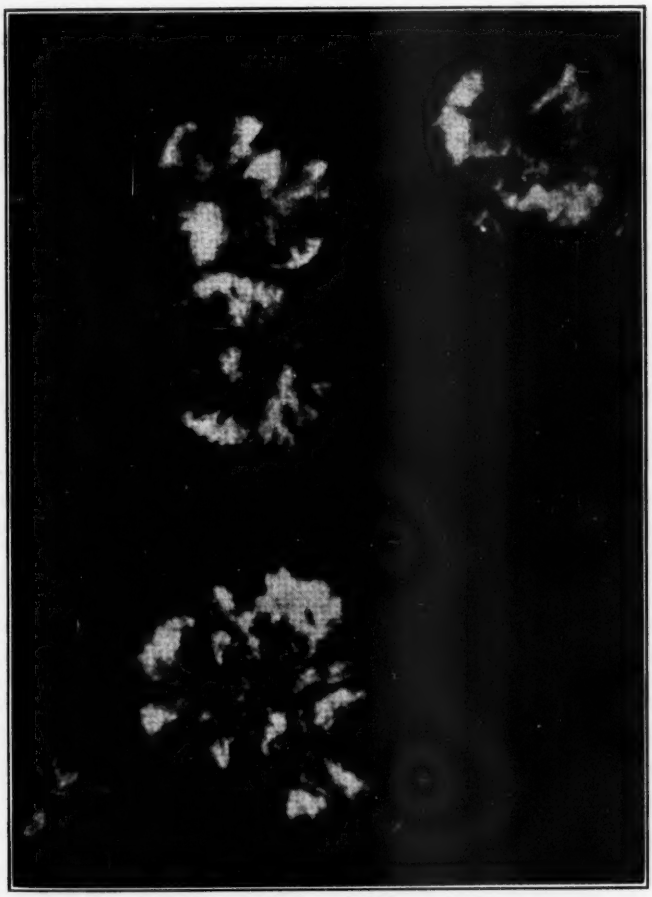

Figure 4—Crystals of Ether-Soluble Rubber Hydrocarbon

Crossed nicols. ×500. The dark cross which is characteristic of spherulites can be readily observed.

are spherulites, clusters of thin needles radiating from a central point. By the birefringence of its individual needles, the cluster appears bright against the dark background. The best organized clusters tend to show the typical spherulitic extinction, a dark radial cross, the arms of which are parallel to the nicol prisms and rotate with them, but in general this phenomenon is not very well marked. This may be caused either by a low state of organization in the clusters or by the needles

not having parallel extinction. It has been mentioned that the latex used in this work was obtained in several different lots. The appearance and properties of the spherulitic clusters did not depend upon the sample of ammoniated latex from which they had been prepared, though the conditions of crystal growth modified the size of the individual needles and their arrangement in the cluster.

Birefringence, or optical anisotropy, is characteristic of three different conditions of matter: (*a*) Viscous liquids or colloidal materials are birefringent when under mechanical strain. Thus a sheet of transparent rubber shows polarization colors when stretched between crossed nicols. This phenomenon is fundamentally different from that described in this report. Furthermore, the conditions under which the clusters were formed are unlikely to result in strains. (*b*) Liquid crystals are birefringent. The great amount of structure observable shows that the clusters of Fig. 4 are not liquid crystals. (*c*) The crystals of five out of six systems of true crystals are birefringent. The crystals of rubber hydrocarbon undoubtedly belong to one of these groups. They are true crystals and appear to offer a means of purifying rubber hydrocarbon.

3. Melting Point

When a birefringent crystal melts, the birefringence disappears abruptly when the structural interrelations of the solid are loosened and before the first signs of flowing can be observed.

The mother liquor was removed from a preparation of rubber crystals and all residual solvent evaporated by evacuating the cell. The photomicrographs in Fig. 3 illustrate the changes in these crystals as they became warmer and establish the melting point of the rubber crystals as higher than +9.5° C. and lower than +11° C. The melting point appeared to be independent of the sample of latex and also not to vary with different preparations of crystals. The conditions of determining the melting point influenced the result somewhat, but not more than would be expected. Table I indicates the results of a varying group of such determinations.

TABLE I

DETERMINATIONS OF THE MELTING POINT OF ETHER-SOLUBLE RUBBER HYDROCARBON

Melting Point (° C.)	Conditions Affecting Accuracy
9.5	Evaporation of ether with water-jet pump
9.8	Evaporation of ether with an oil pump
9.5–11	Very thorough removal of solvent. Evacuation with oil pump continued during entire time that temperature rose. A series of photomicrographs (Fig. 3), shows the condition of the crystals at each significant temperature
9.0–9.5	Replacement of ether with acetone. Melting of crystals determined under acetone
8.0–8.8	Replacement of ether with acetone. Replacement of acetone with Sonstadt's solution[1] diluted with acetone. Melting was determined under this mixture in which the crystals had been immersed at a temperature near their melting point for 4 days

[1] Sonstadt's solution, otherwise known as Thoulet's solution, is a saturated water solution of potassium mercuric iodide. It is used for gravity separations of minerals and occasionally for the determination of refractive indices.

NOTE.—The second and third determinations are believed to be more trustworthy than the others. The third is particularly favored because of the thorough removal of the solvent (the oil pump operated about 3 hours) and because the making of photomicrographs largely removed the personal element from the determination.

That fraction of rubber hydrocarbon which is soluble in ether is therefore a stable liquid at the ordinary temperatures at which rubber is used. Its melting point

has not seemed to depend upon whether it represented the whole ether-soluble component or only that which remained in ether solution after a portion had been precipitated with acetone and discarded.

4. Optical Properties

The largest spherulites which have so far been grown for microscopical examination were about 50 microns (0.05 mm.) across. In these clusters the individual particles were needles about 20 μ long and 1 or 2 μ wide.

The refractive indices of the crystals were determined by immersion[25] in aqueous solutions of potassium mercuric iodide. The method of central illumination was used to indicate the relation between the index of a crystal and the immersing liquid. By adjusting concentrations of the iodide solutions each index of the crystals was matched at $-5°$ C. The index of the corresponding liquid was then determined on an Abbé refractometer at the same temperature.

So far as possible, needles were chosen which were somewhat separated from the clusters. Two indices were determined corresponding to the ϵ and ω of uniaxial crystals. It must not be inferred, however, that the rubber crystals are uniaxial. There was no attempt to obtain an interference figure.

The uncertainty of the determinations is greater than equally careful work would yield in ordinary optical determinations. It is believed to be about ± 0.003. The indices found are

$$\epsilon = 1.535 \text{ at } -5° \text{ C.}$$
$$\omega = 1.583 \text{ at } -5° \text{ C.}$$

Determinations of the optical character of elongation were made with the Johannsen wedge. The crystals have negative elongation. This is consistent with the determined values for ϵ and ω.

The temperature was allowed to rise, and the refractive index of the rubber was determined after the crystals had melted. The refractive index of melted ether-soluble rubber hydrocarbon crystals was found to be 1.525 at 11° C. This corresponds closely with the value found by McPherson,[26] who used large samples of total rubber hydrocarbon.

The microscopical examination of the crystals of rubber hydrocarbon indicates that they are spherulites composed of many fine needles. They have a consistent melting interval of narrow range. The refractive indices of the crystals have been determined. They are higher than the index of the rubber after melting by an amount inconsistent with the "melting" of liquid crystals, but consistent with the melting of true crystals.

V. Determination of the Composition of Pure Ether-Soluble Rubber Hydrocarbon

Henry J. Wing

The ratio of hydrogen to carbon in rubber and rubber hydrocarbon has often been determined. Upon these determinations, in large part, has rested the assumption that rubber hydrocarbon is a polymer of isoprene, which may be represented as $(C_5H_8)_x$. However, this assumption is not entirely justified because of the questionable purity of the substances analyzed and the low precision of many of the reported results. The preparation of pure rubber hydrocarbon in this laboratory offered opportunity to make an accurate determination of the ratio of hydrogen to carbon by the usual method of organic combustion.

1. Apparatus

The combustion furnace and accessories (Fig. 5) were similar to those described by Bruun[27] except that all mercury seals and flow meters were eliminated and all but two of the joints beyond the preheating furnace, *A*, were hermetically sealed. These two, *C* and *D*, were sealed on the outside with DeKhotinsky cement so that the gas stream did not come in direct contact with the cement. In order to obtain suitable blank runs it was found necessary to run the preheating furnace, *A*, at a higher temperature than that of the combustion furnace, *B*.

The absorption tubes were two 75 mm. Schwartz **U** tubes fitted with ground joints on the side arms so that no rubber connections were used. In order to avoid loss due to the action of hot water on the greased joints, the exit tube, *E*, from the combustion tube was bent in a **U** and a small bulb was blown on the outflow side of this **U**. Most of the water from the combustion condensed in the bend of the **U**. The oxygen was allowed to pass until all this water was transferred to the weighing tube in the form of vapor. The weighing tubes were weighed filled with dry hydrogen both before and after the combustion. This made any correction for air buoyancy unnecessary.

A silica-glass sample tube was used in making the combustions instead of an open boat in order to prevent too rapid burning of the rubber. One end of the tube was open and unconstricted. The other end was closed except for a pinhole of such size that the rubber solution would not run through, yet in the combustion furnace oxygen could enter. This tube had two small hooks near the open end so that it could be suspended by a platinum wire for weighing and handling.

2. Preparation of the Sample

The material for analysis had been purified as described in the first part of the paper and put into ether solution. A small portion of this solution was placed in the sample tube. The ether was evaporated from this first small quantity of rubber solution by placing the sample tube containing it in a wide test tube and carefully reducing the pressure. This procedure was repeated until about 0.2 g. of the hydrocarbon had been collected. In order to remove the last traces of solvent the sample tube was then placed in a small glass chamber which was heated to about 100° C. by a glycerol bath and which was evacuated to a low pressure by a mercury vapor pump. The sample was evacuated about 18 hours, then transferred to the balance case and, after standing about 20 minutes, was weighed.

3. Balance, Weights, and Weighing

All weighings were made on a high grade analytical balance sensitive to 0.05 mg. The weights used were calibrated by the weights and measures division of this bureau, and the necessary corrections were applied. The blank runs were reproducible to 0.1 mg. Vacuum corrections were made on the weight of the sample, assumed to have a density of 0.9 g. per cc. However, this has no effect on the carbon-to-hydrogen ratio. Assuming that all the weighings were made to ± 0.1 mg., then the maximum possible relative error in the percentages of hydrogen and carbon, and in the ratio of hydrogen to carbon would be ± 0.2 per cent.

4. Analytical Results

Three different preparations of the ether-soluble rubber hydrocarbon, purified as described in Section II of this paper, were analyzed and the ratio of hydrogen to carbon determined. The results are given in Table II, and are shown graphically in Fig. 6. These results are members of a continuous series, from which the only

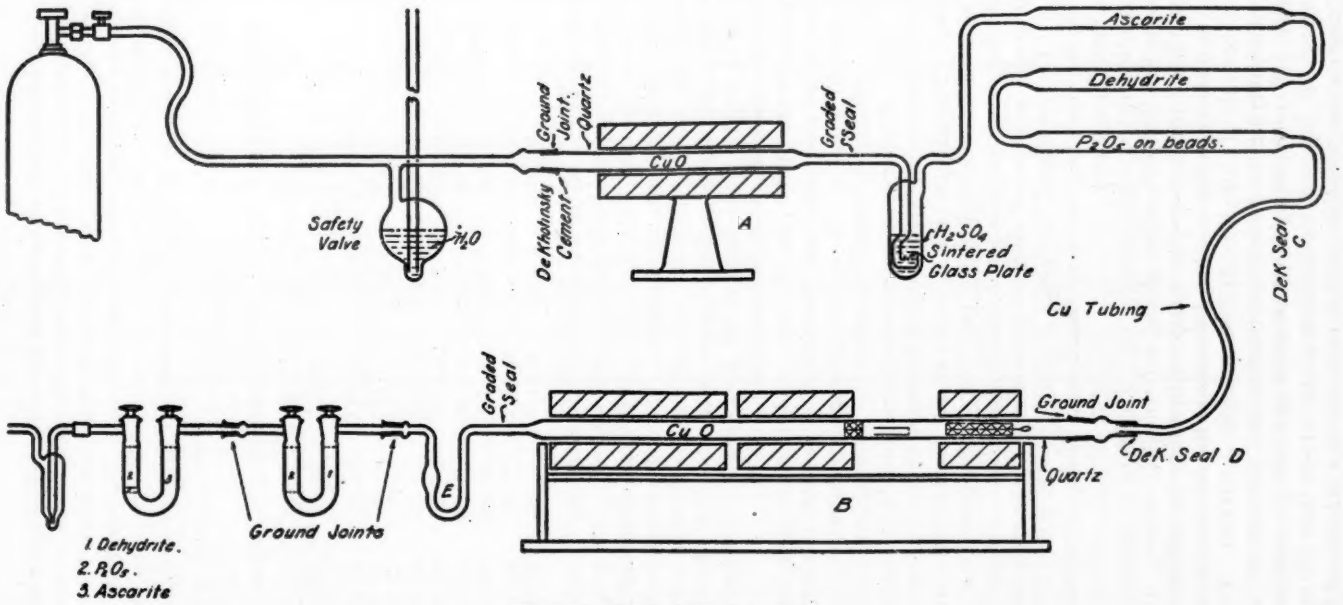

Figure 5—Combustion Apparatus

omissions were those in which the absorption tubes failed to function, either because of stoppage or channeling. Many blank runs were made with the furnace. These were continued until the difference in successive weighings under the conditions of an actual determination was not more than ±0.1 mg. The final ratio of hydrogen to carbon is independent of the weight of the sample. However, as a check on the result the weight of the sample and the percentages of carbon and of hydrogen were determined.

TABLE II

DETERMINATION OF THE RATIO OF HYDROGEN TO CARBON

	Hydrocarbon Taken, G.	H_2O Absorbed, G.	CO_2 Absorbed, G.	Hydrogen Found, Per Cent	Carbon Found, Per Cent	H/C Ratio
Original preparation	0.2009	0.2127	0.6481	11.84	87.98	0.1346
	0.2328	0.2462	0.7516	11.83	88.05	0.1344
	0.2598	0.2732	0.8345	11.77	87.66	0.1343
	0.2358	0.2496	0.7606	11.84	87.97	0.1346
	0.2320	0.2450	0.7475	11.82	87.87	0.1345
Crystallized once	0.2107	0.2232	0.6799	11.85	88.01	0.1346
	0.2390	0.2525	0.7709	11.82	87.97	0.1344
Crystallized three times	0.1365	0.1448	0.4417	11.87	88.25	0.1345
	0.2373	0.1349	0.4111	11.86	88.07	0.1346

These results are figured on the ash-free basis. In every case the ash content was less than 0.1 per cent, practically at the limit of the accuracy of the weighings. The difference between the sum of the hydrogen and carbon percentages and 100 per cent is probably due to the presence of oxygen. Some of the samples were exposed to the air longer than others, which may account for the difference in the sums.

The first step in the interpretation of these results should be the determination of the number of possible compounds which, if subjected to combustion analysis, would give results somewhat in accord with those found.[28]

If we assume for simplicity that the compound does not have more than 100 carbon atoms in the molecule, then the number of possible compounds may be confined to reasonable limits. The ratio of hydrogen to carbon in isoprene or any of its isomers or polymers is 0.13437 based on the International Table of Atomic Weights for 1932. A number of hydrocarbons are possible having less than 100 carbon atoms in the molecule and a ratio of hydrogen to carbon very near to that of the $(C_5H_8)_x$ The diagram (Fig. 6) shows all the possible hydrocarbons in this region. The horizontal scale represents ratio of hydrogen to carbon. Each of the labeled vertical lines represents an individual hydrocarbon. The groups of points in circles represent analyses of different preparations of the ether-soluble rubber hydrocarbon. Group 1 shows the results of analyses of the purified hydrocarbon; group 2, material which had been crystallized once; and group 3, that which had been crystallized three times.

The distribution, in the neighborhood of the C_5H_8 and its polymers, of the hydrocarbons having less than 100 carbon atoms, is fortunately unique. It so happens that none of these hydrocarbons has a ratio of hydrogen to carbon very close to that of C_5H_8 as is shown in Fig. 6. The difference in the ratio of the nearest hydrocarbon on either side of C_5H_8 is $0.13472 - 0.13403 = 0.00069$. This offers the possibility of identifying the rubber hydrocarbon as a polymer of C_5H_8 provided it has less than 100 carbon atoms in the molecule and that the analysis is of the required accuracy. If, however, the molecule contains more than 100 carbon atoms, there still remains the possibility that it may not be a polymer of C_5H_8. Only reliable molecular weight determinations can decide this question.

At present it is not possible to say definitely that the rubber hydrocarbon has a molecule of less than 100 carbon atoms. However, the fact that the material as

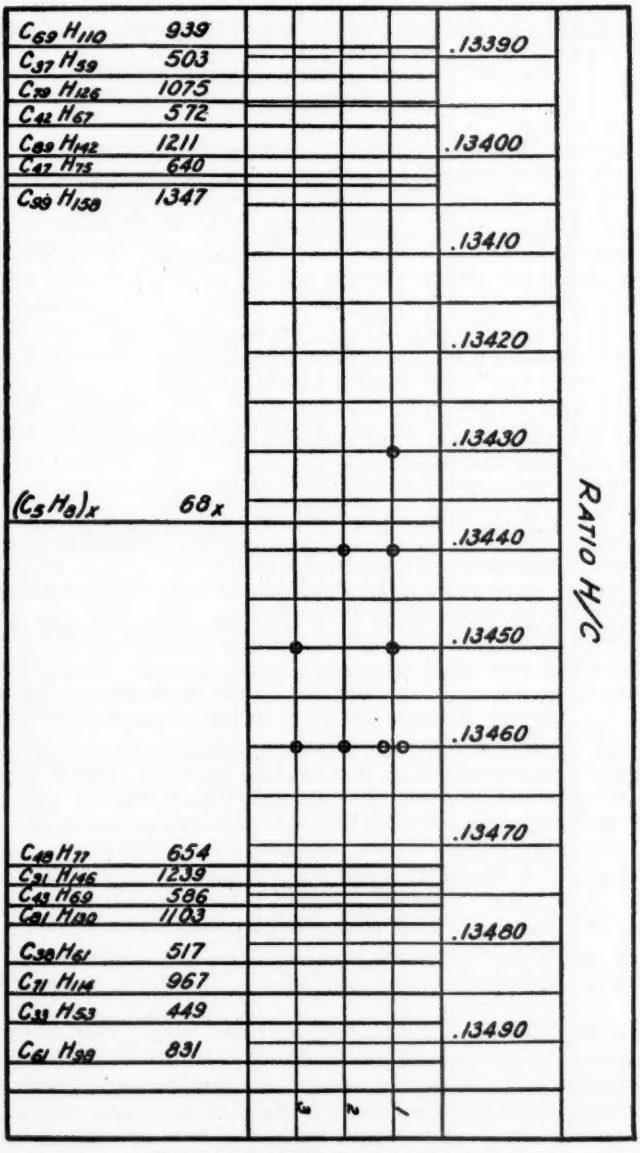

Figure 6—Hydrogen-to-Carbon Ratios

prepared and used in this laboratory crystallizes readily indicates that the molecule is possibly much smaller than has been frequently assumed.

VI. Acknowledgments

The authors acknowledge the technical advice of E. W. Washburn, chief of the chemistry division, throughout the course of this investigation. Harry L. Fisher, of the United States Rubber Co., has furnished us from time to time authentic samples of Hevea latex, and his courtesy is appreciated.

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[15] Pummerer and von Susich, *Kautschuk*, **7,** 117–119 (1931).
[16] DeVries and Beumée-Nieuwland, *Arch. Rubbercultuur*, **9,** 694 (1925).
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The Separation and Identification of Sol Rubber Hydrocarbons

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The hydrocarbon occurring in natural rubber is not homogeneous. This has been demonstrated repeatedly by separation into a more soluble portion, called "sol rubber," and a less soluble portion, called "gel rubber."

A variety of methods, all based on solubility difference, have been employed to bring the separation about. The best known are: (1) the slow diffusion of rubber in petroleum ether, a method originated by Caspari[1] and improved by Feuchter[2] and by Pummerer and Miedel,[3] and (2) the separation by means of absolute ether into an "ether-soluble portion" and an "ether-insoluble portion."[4] However, the same methods in the hands of different experimenters have given discordant results, and the conclusions have been debatable. For instance, Hauser[5] found that after a first separation, rubber can be refractioned again into sol and gel rubber and from this he concludes that sol and gel form an equilibrium mixture which will automatically be regained when one of its components is decreased or eliminated. Whitby[6] observes that different solvents furnish different ratios of sol/gel, and he concludes that the rubber hydrocarbon is a mixture of molecules of varied sizes.

It appears that the investigators employing diffusion methods implicitly assumed that sol and gel rubber were not miscible in each other, and that, in its essence, the separation was analogous to that of sugar from sand by water.

The apparently incoherent results obtained by diffusion separation are rendered quite reasonable when the mutual solubility of sol and gel is taken into account. A single diffusion of rubber in a given solvent establishes a two-phase system, each phase of which contains both sol and gel rubbers, but in different proportions. In other words, diffusion accomplishes only a partial separation.

As a means of coarse separation, diffusion is quite acceptable; but if complete separation is desired, refractionation until the fractions are no longer altered is essential. For this purpose, diffusion is unsatisfactory, because the length of time required to reach equilibrium is sufficient to allow the rubber solution to degrade.

Proponents of the diffusion methods may argue that degradation occurs only in the presence of oxygen, and that a fractionation by repeated diffusion in an inert atmosphere cannot be criticized. This may be true. But it must be borne in mind that, given sufficient time, minute quantities of oxygen are sufficient to cause considerable degradation, and the complete elimination of oxygen is a difficult experimental accomplishment. Hence, the diffusion method is not practical for refractionation.

A method of fractionation based on precipitation at different temperatures has been described and advocated in a series of previous papers.[7] This method is not subject to the same criticism as the diffusion method, because it establishes equilibrium in a short period of time. The degradation which occurs, despite the careful elimination of oxygen during the procedure, is so slight that it does not obscure the results nor vitiate their interpretation.

Method of Separation

The temperature differential method is based on the different solubilities of the hydrocarbons of rubber in a certain solvent, at a certain temperature. It makes

use of the fact that mixtures of rubber, benzene, and alcohol are single-phased within certain limits of concentration and temperature, and, upon cooling, separate into two phases at a definite temperature. One of the phases contains the sol rubber in preponderant quantity, the other contains most of the gel rubber. By repeating the process the preponderant component of one of the phases is progressively freed of the principal component of the other phase. The experimental details and the efficiency of the procedure are outlined in the appendix.

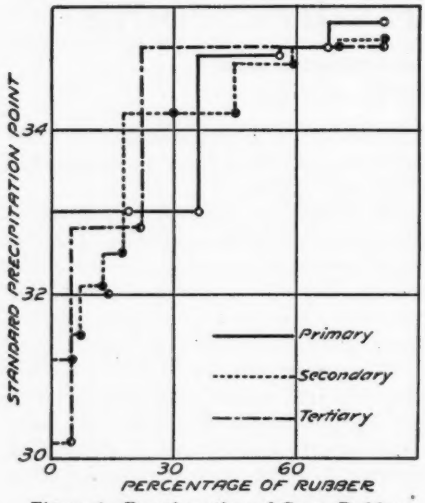

Figure 1—Fractionation of Crepe Rubber

Criterion of Identification

No fractional procedure of any kind can be satisfactorily performed without a criterion to judge the progress of the fractionation. The measurement of a physical constant such as density, refractive index, melting point, etc., is generally used: in the case of rubber, this is impractical, and consequently a specially standardized physical constant has been devised and called "standard precipitation point," or by abbreviation, "s. p. p."

The standard precipitation point is defined as the temperature at which a slowly cooled mixture of 0.85% of rubber, 28.55% absolute alcohol, and 70.60% benzene shows a sudden increase of turbidity. The experimental details needed to measure an s. p. p. are given in the appendix.

Results

The application of the temperature fractionation method, controlled by adequate s. p. p. determinations to a variety of rubber specimens, has given the results graphically represented in Figs. 1 to 4. The mode of representation is the same as for an Engler distillation.

In addition to the preceding cases, a sample of smoked sheet was fractioned: the s. p. p. of its sol fraction was found to be 34.8°.

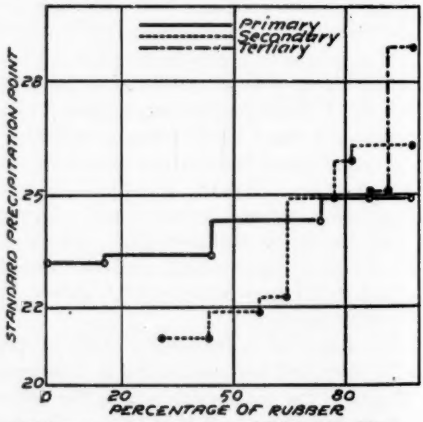

Figure 2—Fractionation of Milled Rubber

Irrespective of their source, the sol rubbers present the same characteristics, *i. e.*, they are white, translucent, semi-plastic, elastic substances. Tackiness is absent from s. p. p. 33° upward, but is quite noticeable at s. p. p. 32° or lower. Pure sol rubbers are unstable at room temperature. Degradation is detectable after a few days, despite precautions against oxygen. Storage in solid carbon dioxide retards degradation but does not prevent it com-

pletely. No tendency to form gel rubber or equilibrium mixtures thereof has been observed.

Interpretation

A comparison of the results reported in Fig. 1 (pale crepe) and Fig. 2 (milled rubber) shows that extreme milling degrades both sol and gel rubbers. Hence it is

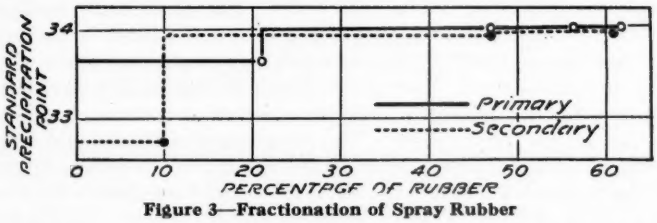

Figure 3—Fractionation of Spray Rubber

reasonable to assume that the presence of components of low s. p. p. in Fig. 1 is due to the sheeting process undergone by the rubber before being baled. With this in mind, the results reported in Fig. 3 (sprayed rubber) indicate that nature produces only one sol rubber in a given specimen. This does not mean that natural sol rubber is a single invariable compound; variations occur between sol rubbers of different specimens. The limited number of specimens studied, and their insufficiently known history preclude, at the present time, any conclusion as to the factors involved in this variability. Seasonal, soil, and climatic conditions suggest themselves as suitable for continued research.

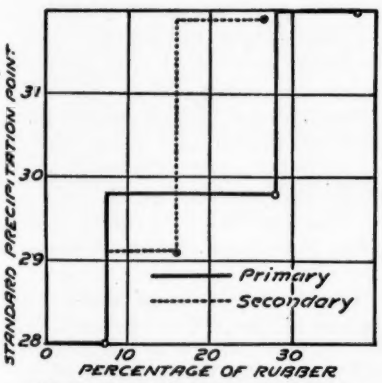

Figure 4—Fractionation of Guayule Rubber

Conclusions

(1) Nature produces a definite sol component in any single specimen of natural rubber.

(2) The sol component can be separated and purified by refractionation methods.

(3) Purified sol rubber retains the physical properties of natural rubber; it can be vulcanized to yield a product of superior quality.

(4) No experimental evidence exists to justify the opinion that rubber is a two-phase system.

(5) Sol rubber and gel rubber are mutually soluble.

Appendix

Determination of the Standard Precipitation Point, s. p. p.—A 1.288 g. sample of the rubber (free from solvent) is placed in a 250-cc. Erlenmeyer flask. One hundred cc. of C. P. benzene is added. The flask is set away in the dark, under CO_2, until complete solution is obtained. To this solution, warmed to about 50°, is added a hot mixture of 27 cc. of benzene and 56 cc. of absolute alcohol, and the whole is stirred and intermittently warmed until entirely clear. A calibrated thermometer reading tenth degrees C. is placed in it and it is allowed to cool. When the mixture becomes suddenly turbid, the temperature is read. This is the experi-

mental precipitation point. It is reproducible to ±0.1°. After checking the point, the flask is equipped with a bent tube carrying a water jacket on its downward branch. This branch delivers into a 250-cc. receiver cooled in ice; the receiver is in turn connected to a second one cooled in a mixture of carbonic snow and acetone, to assure the recovery of all solvents during distillation. Atmospheric moisture is kept out of the system by means of a calcium chloride tube. While passing a slow stream of purified CO_2 through the system, the solvents are distilled with a steam bath. The distillate is weighed and its refractive index is measured in a Pulfrich refractometer at 20.0°. From a previously constructed curve, the composition of the distillate is read. The rubber sample is weighed as soon as the distillation is finished, and its increase in weight, regarded as benzene, is added to the amount of benzene in the distillate. The percentages of alcohol and benzene are thus determined with accuracy; they can be duplicated to 0.1%. By means of the chart Fig. 2, paper VII,[7] the experimental precipitation point is then corrected to standard conditions, *viz.*, 28.55% alcohol and 0.85% rubber. This is the s. p. p.

Fractionation Procedure.—Two hundred and fifty grams of crepe rubber with a nitrogen content of 0.25% were dissolved in 8083 g. of benzene heated to about 50°. A hot mixture of 4500 cc. of absolute alcohol and 1400 cc. of benzene was added slowly, with constant stirring, until complete solution was obtained. The critical temperature, determined on a 50 cc. sample, was 43.0°. The mixture was then held at 42.0° in a thermostat for one hour. At the end of this period the mixture was no longer homogeneous, but consisted of a completely settled gel phase and a clear supernatant liquid. This liquid was decanted, then cooled in an ice-bath, and yielded 52.9 g. of rubber hydrocarbon, hereafter designated as A_1. After removal of the A_1 rubber, the liquid was warmed and poured back on the gel phase. By warming and stirring, the gel phase was caused to dissolve, and a clear solution was then obtained. A sample of this solution exhibited a critical point of 43.5°. Consequently, the solution was placed in a thermostat regulated at 42.5° for one hour, and the above procedure was repeated. This time 30.5 g. of rubber hydrocarbon was obtained, called A_2 hereafter. Two repetitions of these operations yielded fractions A_3 and A_4.

After the fraction A_4 had been collected, it was found that the gel phase would no longer dissolve completely in the alcohol-benzene mixture, even when the solvent was brought to its boiling point. Consequently, the insoluble matter was separated from the solvent; the solvent, upon cooling, yielded a fraction called A_5. Finally, the insoluble matter was extracted in a Soxhlet extractor with benzene. The material obtained from the benzene was called A_6, while the insoluble matter was called B.

Efficiency of the Procedure.—The efficiency of the separation method is illustrated as follows. A 10-g. specimen (s. p. p. 35°) and a 10-g. specimen (s. p. p. 28.9°) were dissolved in the same batch of benzene and separated by fractional precipitation. A single fractionation yielded 11.5 (s. p. p. 34.9°), 8.5 g. (s. p. p. 28.5°).

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[4] Pummerer, *Kautschuk*, **1927**, 233; Pummerer and Pahl, *Ber.*, **60**, 2152 (1927).
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[6] *Trans. Inst. Rubber Ind.*, **5**, 184 (1929); **6**, 40 (1930).
[7] Midgley, Henne, and Renoll, *J. Am. Chem. Soc.*, **53**, 2733 (1931); **54**, 3343, 3381 (1932).

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Structural Viscosity in Some Lyophilic Sols

II. Rubber Sols

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Abstract

The relative viscosities of sols of natural and purified rubber in benzene were measured at varying pressures, using the overflow viscosimeter. Deviations from Poiseuille's law to varying extents were found in all cases, with regions of structure and turbulence at various pressures. The limiting concentrations above which structure is evident and Poiseuille's law is not obeyed were found to be in agreement with those calculated by Staudinger on the basis of his theory of the relation between the viscosity and molecular weight of polymeric molecules. Exposure to ultra-violet light was found to decrease considerably the viscosity of a sol of purified rubber.

The equation of Einstein expressing a linear relation between specific viscosity and the volume occupied by the solute, based partly upon the assumption of non-deformable spheres, has been found to hold for certain sols, *e. g.*, mastic. It has been found to fail utterly, however, in the case of such sols as gelatin and rubber. The relative viscosity of such sols increases enormously with increase in concentration, and on the basis of Einstein's equation, attempts at calculations of the volume occupied by the solute often yield figures many times greater than the actual volume of solvent used.

Staudinger[2] has found the following empirical relation to hold for various polymeric series,

$$\frac{\eta_{sp}}{c} = K.M,$$

where η_{sp} is the specific viscosity, c the concentration, M the molecular weight, and K a constant for any one series in the same solvent.

Assuming that the extent of solvation is small, possibly only an adsorption film, Staudinger considers that the effective volume of a long-chain molecule is that of a short cylinder encompassing the rotatory movements of the molecule. Upon this assumption, the effective volume occupied by the molecule must be proportional to the square of the molecular weight or chain length. In a dilute sol containing solute molecules of less than a certain size, the volume of solvent available is sufficient for free movement of the particles. In a sol of the same concentration containing very long molecules, however, the number of molecules decreases inversely as the chain length, but the effective volume increases as the square of the chain length, and a condition is attained where the volume of solvent available no longer suffices for free movement of the particles. Staudinger has calculated the effective volumes of various high polymers and the limiting concentrations above which normal solution changes to "gel solution."

It is evident that this condition of mutual hindrance in the movement of solute particles must be synonymous with the structural region, discussed elsewhere,[1] where there is no conformity with Poiseuille's law. The extent of solvation is considered by most workers to be very great. However, the interaction between the bound solvent in the outer parts of the spheres of attraction of two molecules,

from the point of view of viscosity, is unknown. Under these conditions also, the magnitude of the force binding the liquid at some distance from the hydrocarbon chain is very uncertain.

In order to test the theory of Staudinger from the point of view of the critical concentrations above which normal solution is no longer possible, the viscosity of a number of rubber sols was investigated by means of the overflow viscosimeter.

Figure 1 shows the viscosity-pressure curves of sols of various concentrations of acetone-extracted smoked sheet. Neglecting for the moment the initial rise in viscosity, it is seen that the relative viscosity is independent of the pressure with a concentration of 0.19%, but the structural effect is very marked at a concentration of 0.38%. Staudinger[3] gives 0.2% as the limiting concentration in the case of raw *Hevea* rubber.

Figure 2 shows the viscosity-pressure curves for sols of various concentrations of purified rubber. The rubber was purified by the diffusion method (described in the experimental section) after acetone extraction, and showed no nitrogen present by the sodium fusion test. The sol of 0.42% concentration shows no structure, and the sol of 1.06% concentration shows marked structure. The limiting concentration given by Staudinger[3] for a rubber sol purified according to the method of Pummerer is 0.61%. This figure is for the more readily soluble portion of the rubber (the so-called sol-rubber) as purified according to Pummerer. In the present instance, only the most readily diffusible portion of the rubber was used, representing only about 5% of the total weight of rubber employed. In order of magnitude, at least, the results of these viscosity measurements are in agreement with the theory of Staudinger.

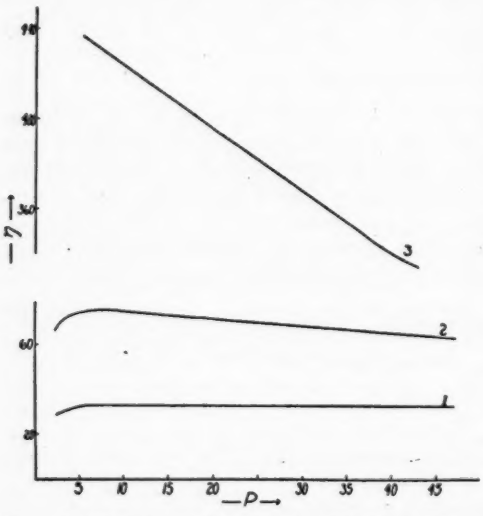

Figure 1—Viscosity of Sols of Natural Rubber. Concentrations: 1, 0.19%; 2, 0.38%; 3, 0.96%

Figure 3 shows the effect of exposure to ultra-violet light (6 hours) of sols of natural and the purified smoked sheet. The sols were contained in loosely stoppered quartz flasks with air above the sol. It is well known that the removal of nitrogenous matter from the rubber results in a large decrease in viscosity, but it is evident that the structure is due to the hydrocarbon. The effect of exposure to ultra-violet light also causes a decrease in viscosity, not only in the sol of natural rubber but also in that of the purified hydrocarbon, and therefore it may be concluded that the effect is chiefly, if not entirely, upon the hydrocarbon itself.

In nearly all of these viscosity-pressure curves for rubber sols, it will be noticed that the first part shows an increased viscosity with rise in pressure. On the basis of long unbranched hydrocarbon chains, this initial rise is very difficult of explanation. On the other hand, assuming the presence of branched chains, there is a possibility of initially increasing interference with the tendency toward orientation of the molecules.

Experimental

Natural smoked sheet was extracted with dry acetone for ten days at about 30° C., dried *in vacuo* and sols were prepared in pure benzene at room temperature. The viscosities were measured with the overflow viscosimeter immersed in a thermostat kept at 30° C. The capillary was attached at both ends by well-fitting corks

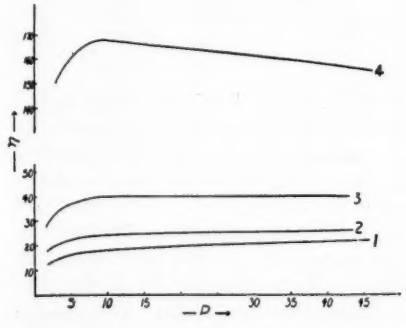

Figure 2—Viscosity of Sols of Purified Rubber. Concentrations: 1, 0.11%; 2, 0.21%; 3, 0.42%; 4, 1.06%

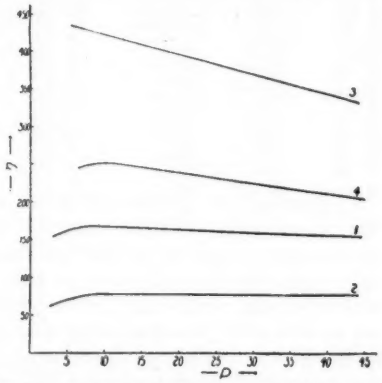

Figure 3—Effect of Ultra-Violet Light on Viscosity of Rubber Sols. Purified Rubber, Concentration 1.06%: 1, before exposure; 2, after exposure. Natural rubber, concentration 0.96%: 3, before exposure; 4, after exposure

coated with a lacquer insoluble in benzene. The method of calculation has been given elsewhere.[1]

In the following condensed tables, P is the pressure in cm. of solution, V the velocity of flow in cc. per 10 sec., and $\eta = \frac{P}{V}$ the relative viscosity. Tables I, II, and III express the results for natural rubber sols of various concentrations.

TABLE I

VISCOSITY OF SOL, 0.96%

P	V	η
43.82	0.131	334.0
37.67	0.100	376.7
31.97	0.089	358.6
27.10	0.073	369.6
23.12	0.060	385.4
19.83	0.050	396.6
17.12	0.042	410.9
14.82	0.036	413.5
12.85	0.031	416.6
11.34	0.027	424.9
9.19	0.022	427.2
7.99	0.019	427.9
6.96	0.016	430.5
6.06	0.014	432.8
5.29	0.012	434.8

TABLE II

VISCOSITY OF SOL, 0.38%

P	V	η	P	V	η
45.5	0.71	64.3	8.33	0.11	75.7
41.5	0.64	65.0	7.69	0.10	74.4
37.85	0.58	65.8	7.10	0.10	73.4
34.60	0.52	66.7	6.53	0.09	72.5
31.63	0.47	66.8	6.03	0.08	75.4
28.92	0.43	67.3	5.58	0.075	74.4
26.48	0.39	68.5	5.14	0.070	73.4
24.28	0.35	69.7	4.75	0.063	75.0
22.30	0.32	70.1	4.38	0.062	71.0
20.46	0.29	70.1	4.01	0.057	70.8
18.80	0.26	71.4	7.50	0.050	74.0
17.30	0.24	71.6	3.41	0.048	70.6
15.91	0.22	72.9	3.13	0.043	72.2
14.69	0.20	72.7	2.89	0.043	66.7
13.50	0.19	72.3	2.62	0.040	65.5
12.45	0.17	74.7	2.41	0.035	68.0
11.50	0.15	75.0	2.20	0.033	66.0
10.61	0.14	74.0	2.01	0.032	63.5
9.78	0.13	73.4	1.83	0.028	64.6
9.01	0.12	74.0			

TABLE III

VISCOSITY OF SOL, 0.19%

P	V	η	P	V	η	P	V	η
45.60	1.42	32.2	15.15	0.46	32.9	5.09	0.16	31.8
41.50	1.28	32.3	13.82	0.42	32.9	4.62	0.15	30.8
37.90	1.15	32.9	12.63	0.38	32.9	4.20	0.14	30.0
34.60	1.06	32.6	11.53	0.35	33.3	3.81	0.123	30.9
31.55	0.98	32.3	10.56	0.32	33.0	3.48	0.110	31.6
28.75	0.88	32.8	9.62	0.29	32.8	3.15	0.110	28.7
26.30	0.81	32.5	8.80	0.26	33.4	2.83	0.100	28.3
23.90	0.74	32.2	8.04	0.25	32.6	2.56	0.087	29.6
21.85	0.67	32.8	7.33	0.23	32.3	2.31	0.080	28.9
19.90	0.61	32.5	6.68	0.20	33.4	2.09	0.070	29.9
18.17	0.55	32.8	6.13	0.18	33.5	1.90	0.067	28.5
16.58	0.50	32.9	5.58	0.17	32.2			

A quantity of acetone-extracted smoked sheet (treatment described above) was placed in large flasks together with a sufficient volume of pure benzene to leave a supernatant layer after swelling of the rubber. The rubber was allowed to diffuse into the liquid for two periods of four days each with withdrawal of supernatant sol and replacement with pure solvent after each period. Care was taken not to shake the vessels during this treatment. The concentration of solute was determined on an aliquot portion and the sol tested for nitrogen by the sodium fusion test. The latter yielded negative results. Approximately 5% of the total weight of rubber diffused into the benzene during this treatment. The relative viscosities of sols of various concentrations at varying pressures are shown in Tables IV, V, VI, and VII.

TABLE IV

VISCOSITY OF SOL, 0.11%

P	V	η
38.85	1.80	21.6
29.22	1.42	20.6
21.72	1.09	19.9
15.97	0.83	19.3
11.69	0.62	18.8
8.47	0.47	18.0
6.06	0.35	17.3
4.26	0.26	16.4
3.21	0.24	13.4
1.70	0.127	13.4
1.06	0.09	11.8
0.49	0.06	8.2

TABLE V

VISCOSITY OF SOL, 0.21%

P	V	η
40.66	1.54	26.4
32.32	1.25	25.8
25.56	1.01	25.4
20.16	0.81	25.0
15.87	0.64	24.9
12.47	0.51	24.6
9.78	0.40	24.4
7.60	0.33	23.4
5.86	0.26	22.5
4.50	0.21	21.4
3.40	0.16	21.3
2.74	0.133	20.6
1.71	0.097	17.6
1.21	0.072	16.8
0.80	0.063	12.7

TABLE VI

VISCOSITY OF SOL, 0.42%

P	V	η
41.22	1.02	40.4
35.31	0.89	39.8
30.56	0.76	40.2
26.32	0.66	40.0
22.68	0.56	40.5
19.58	0.49	40.0
16.89	0.42	40.2
15.24	0.36	42.3
12.57	0.31	40.5
10.84	0.26	41.2
9.36	0.23	40.7
8.01	0.21	39.1
5.46	0.145	37.7
3.95	0.109	36.2
2.81	0.083	32.6
1.95	0.063	31.1
1.28	0.05	25.6

TABLE VII

VISCOSITY OF SOL, 1.06%

P	V	η	P	V	η	P	V	η
42.7	0.27	156.2	16.64	0.101	165.0	5.57	0.034	162.6
40.39	0.26	156.0	13.39	0.082	163.8	4.44	0.029	154.2
32.21	0.20	160.2	10.79	0.065	165.6	3.52	0.023	153.0
25.79	0.16	161.4	8.68	0.052	168.0	2.77	0.018	158.4
20.67	0.126	163.8	6.96	0.047	148.8	1.93	0.015	133.2

Two of the sols, one of natural and one of the purified rubber, were exposed for six hours to ultra-violet light in a mercury arc fluorescence cabinet. The sols were contained in loosely stoppered quartz flasks with air above the sol. A blue

filter was used to avoid rise in temperature. The relative viscosities of these sols after exposure are shown in Tables VIII and IX.

TABLE VIII

VISCOSITY OF PURIFIED RUBBER SOL, 1.06%

P	*V*	η	*P*	*V*	η	*P*	*V*	η
42.8	0.56	77.1	15.82	0.21	77.2	5.61	0.077	73.2
39.65	0.53	75.5	14.64	0.19	77.7	5.18	0.072	72.3
36.70	0.47	78.6	13.57	0.18	77.5	4.76	0.065	73.2
34.05	0.43	78.6	12.55	0.16	76.8	4.40	0.063	69.6
31.50	0.41	77.7	11.61	0.15	76.6	4.00	0.062	64.8
29.20	0.37	79.6	10.74	0.14	76.7	3.66	0.057	64.8
27.10	0.35	78.2	9.93	0.132	75.4	3.33	0.053	62.5
25.05	0.32	77.4	9.17	0.122	75.4	3.03	0.047	63.0
23.23	0.30	78.3	8.48	0.115	73.8	2.78	0.043	64.2
21.50	0.28	78.2	7.80	0.107	73.2	2.52	0.040	63.0
19.93	0.25	79.2	7.20	0.097	74.7	2.30	0.037	62.7
18.48	0.24	78.0	6.65	0.092	72.6	2.08	0.035	59.5
17.10	0.22	77.6	6.10	0.087	70.4			

TABLE IX

VISCOSITY OF NATURAL RUBBER SOL, 0.96%

P	*V*	η	*P*	*V*	η	*P*	*V*	η
45.55	0.23	197.5	20.40	0.086	238.5	9.80	0.040	248.4
41.70	0.20	207.9	18.93	0.078	241.6	9.13	0.036	252.9
38.33	0.18	214.9	17.59	0.073	241.7	8.49	0.034	250.6
35.28	0.16	218.2	16.31	0.068	240.7	7.90	0.033	241.0
32.52	0.15	221.8	15.16	0.062	245.9	7.32	0.031	239.6
30.00	0.13	225.0	14.09	0.057	246.2	6.81	0.027	250.2
27.73	0.12	229.0	13.10	0.053	248.2	6.35	0.026	248.4
25.64	0.11	230.8	12.19	0.049	249.3	5.90	0.024	241.4
23.73	0.10	234.7	11.35	0.046	249.1			
22.01	0.093	237.2	10.55	0.043	246.6			

References

[1] Gallay, *Can. J. Research*, **7**, 662 (1932).
[2] Staudinger, *Z. angew. Chem.*, **45**, 276, 292 (1932).
[3] Staudinger, *Kautschuk*, **6**, 153 (1930).

[Translated for RUBBER CHEMISTRY AND TECHNOLOGY from Comptes Rendus des Séances de l'Académie des Sciences, Vol. 196, No. 24, pages 1796–1797, June 12, 1933.]

The Limiting Degradation of Rubber Solutions

Paul Bary and Émile Fleurent

In our preceding papers [cf. *Compt. rend.*, **192,** 946 (1931); **193,** 852 (1931); **195,** 665 (1932)] we have pointed out that the degradation of solutions of rubber in xylene at concentrations of one to five per cent and at temperatures of 44° and 92° C. in sealed tubes tends toward a limit which depends upon the concentration and upon the temperature.

One of the series of experiments carried out to determine the conditions under which this degradation takes place was continued to the point where the viscosity of the solutions reached a constant value in every case. With five per cent rubber solutions this result was obtained after a time which was practically of the order of 10,000 hours of heating, while the more dilute were the solutions and the higher was the temperature, the shorter was this time.

At this limit, the viscosity of the solution reaches a final constant value for the particular temperature. It is therefore of interest to compare the law of viscosity as a function of the concentration of solutions, represented in its final form by the general formula of Arrhenius, for the viscosity as a function of the concentration of lyophylic colloidal solutions:

$$\log \eta = KC$$

where η is the ratio of the viscosity of the solution to the viscosity of the pure solvent, C the concentration and K a constant.

The accompanying table gives the limiting values of η_∞ found at 44° and at 92° C. for six different concentrations.

Concentration C	η_∞		Log η_∞	Log η_∞ at 92°	
	At 44°	At 92°	at 44°	Found	Calculated
0.01	4.99	1.94	0.70	0.287	0.368
0.015	7.30	3.27	0.86	0.514	0.352
0.02	20.5	5.45	1.31	0.736	0.736
0.03	42.7	11.7	1.63	1.068	1.104
0.04	133.0	30.0	2.12	1.477	1.472
0.05	196.0	77.8	2.29	1.891	1.840

According to the Arrhenius formula, the values of the logarithms of the viscosities should be proportional to the concentration. This condition appears to be fairly well satisfied by solutions which are maintained at a temperature of 92°, as is shown by the last column of the table, which gives the value calculated according to the formula:

$$\log \eta_\infty = 36.8\, C$$

with an approximation which is satisfactory for this type of experiment, considering the difficulties which were discussed in our preceding paper.

On the contrary, at 44° the experimental values of log η_∞ do not lie on a straight line, but on a curve concave to the axis of the concentrations. A similar observation has also been made by Duclaux and Nodzu for solutions of nitrocellulose in methylethylketone.

It is difficult to explain the causes of the deviations which were found in a rather large number of experiments, each of which corresponded to a particular sealed tube. It would appear that, under the prolonged action over a period of thousands of hours of heating, even slight traces of certain impurities originating perhaps in the walls of the tubes, perhaps in the solvent or even in the rubber itself, are sufficient to cause differences, sometimes of considerable extent, in the value of the viscosity. The series of experiments carried out at 92°, which conforms very well with the linear law of Arrhenius, is from this point of view much more satisfactory than the curve obtained from the series of experiments at 44° C.

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 9, No. 3, pages 34–37, March, 1933; No. 4, pages 49–52, April, 1933.]

The Autoöxidation of Rubber Latex

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The autoöxidation of rubber has been studied frequently and exhaustively,[1] whereas that of latex[2] stabilized with ammonia has been studied relatively little. It seemed worth while, therefore, to study the behavior of latex more closely, not only because of its increasing technical importance, but also because many influences such as a change in the p_H value can be examined more conveniently with it than with commercial rubber. Latex has, to be sure, a very complex structure, and account must be taken of the the fact that it contains other substances which are also oxidized. Even if these substances occur only in small concentrations, they can still affect the rate of oxidation of rubber noticeably.[3] Since they can be separated only by an exhaustive operation, it appears to be reasonable and necessary first of all to study the behavior of latex as such.

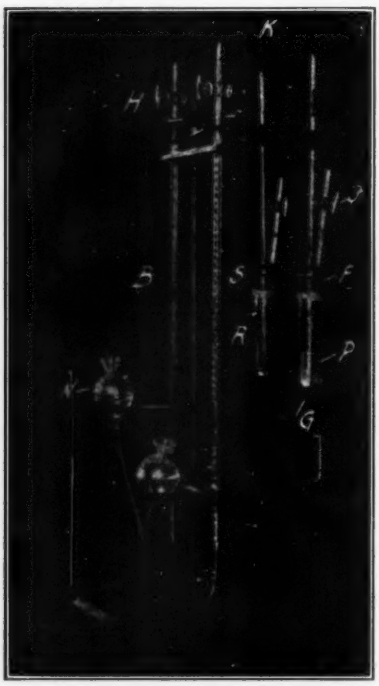

Figure 1

I. Experimental Procedure and Method of Measurement

The autoöxidation of rubber latex was measured by determining volumetrically the quantity of oxygen absorbed as a function of the time. The method used was based upon that of Peachey.[4] The apparatus is shown in detail in Fig. 1.

The reaction vessel R is connected with the graduated burette B by the ground glass joint S and the capillary K by means of two springs F. It contains, besides plates P, on which are the latex films to be studied, a small cylindrical vessel, G. The latter is filled with solid potassium hydroxide to catch the carbon dioxide formed by oxidation.[5] Both capillary stopcocks H and J, of which H is a 3-way stopcock, are used for the purpose of filling the apparatus with oxygen. H is also used to refill the burette during the course of the experiment without interrupting the experiment. A leveling flask, N, makes possible an equalization of the difference in pressure resulting from absorption of oxygen in the apparatus, and serves also to give an exact leveling of the surface of the liquid while readings are being taken. Dilute potassium hydroxide is used for the sealing liquid.

The reaction vessels in groups of four in a support were placed in thermostats for the duration of the experiment. (Figure 1 shows only two vessels.) The

experiments were carried out in carefully regulated thermostats, the temperature of which was 85° C. ± 0.05°. All measurements were carried out in a dark hood with exclusion of both direct and diffused light.

The experiments were carried out in the following way: Ammoniated *Hevea Brasiliensis* latex, containing originally 36.02 per cent of dry substance, was diluted with an equal volume of distilled water. One cubic centimeter samples of this product, containing 18.01 per cent dry substance, were spread uniformly with the aid of a glass needle on four glass plates, each of about 3 x 12 cubic centimeters area.

As far as the influence of the surface on the rate of oxidation is concerned, Kohman[6] has shown that in the case of ordinary commercial rubber the quantity of oxygen absorbed per unit time is proportional to the surface area, *i. e.*, it increases with increase in the surface area as long as the layer is relatively thick, but is independent of slight variations in the surface area. The influence of the surface no longer plays any part when the surface becomes so great and the thickness of the rubber layer so small that diffusion through the rubber layer takes place practically instantaneously. This was the case in our experiments, as will be shown by a typical case.

In measurements made with salts of heavy metals, four cubic centimeters of salt solution were added dropwise to the latex on the plate so that it was mixed as uniformly as possible with the latex.

When protective substances were used, two cubic centimeters of a solution of the substance were added in the same way before the heavy metal salt was added.

The plates were dried 48 to 72 hours in the desiccator *in vacuo* over calcium chloride. In this way four identical films were obtained with a total area of 150 square centimeters and a content of dried latex of approximately 0.18 gram.

Two plates were placed together with the film on the outside, and a pair of such plates was then placed in the reaction vessel on each side of the tube containing solid potassium hydroxide, and the reaction vessel was fastened to the ground glass joint with two clamps. A strong current of oxygen was passed through the apparatus for 60 to 120 seconds and the stopcocks were closed after the air had been removed. The flask was then filled with oxygen. With the aid of the leveling flask and the rear stopcock, the surface of the liquid in the burette was set at the zero mark, and the reaction vessels were placed in the thermostats.

As far as the influence of the temperature on the rate of oxidation is concerned, Williams and Neal[7] showed that the van't Hoff temperature coefficient also holds for the rate of autoöxidation of rubber. These investigators found that absorption of oxygen doubles with a rise of about 7° to 10° C. in the temperature of the reaction.

Since the vessels become warm in the thermostat, the level of the liquid in the burette first sinks, reaches a minimum after a definite time, and then the resulting absorption of oxygen causes a reverse movement. If the volumes measured in this way (Table 1, column 1) are plotted as a function of the time, curves of the type of curve *A* (Fig. 2) are obtained.

The values in Table I as well as those in Figs. 2 and 3 are for latex films which were prepared from one cubic centimeter of the latex preparation described above and four cubic centimeters of a 10-millimolar copper sulfate solution. In so far as they are negative, they indicate that in the beginning, as a result of the heating, a volume increase took place which gradually decreased as a result of absorption of oxygen until the level of the liquid reached the starting point. The absorption of oxygen from this point shows positive values, and can be followed progressively, since the burette can be replenished with oxygen without having to interrupt the experiment.

In order to avoid the difficulties which are encountered, and to determine the nature of the curves, it would be necessary to compensate for the temperature, as was done by Warburg[8] in his work on cell respiration. In this case, however, the first part of the curve would be eliminated, and it would then be impossible to know the initial course of the reaction. Since as a matter of fact the reaction is autocatalytic, with an induction period at the beginning, it is necessary to take this into account. The method is therefore not to be recommended.

Instead another method was adopted. One of the reaction vessels was filled with nitrogen instead of oxygen, and here too the change in the level of the liquid was followed. In this case only a drop to a minimum was observed, whereupon the level of the liquid ordinarily rose somewhat until—aside from slight changes caused by variations in temperature and in pressure—it finally remained at a constant level (see Table I, column 2 and curve *B* in Fig. 2).

The slight rises observed at times in the nitrogen curve are probably caused by the evaporation of traces of water in the reaction vessel on heating to 85°. After the normal vapor pressure for this temperature is reached, the greater part of the

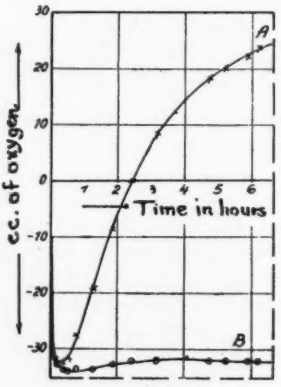

Figure 2

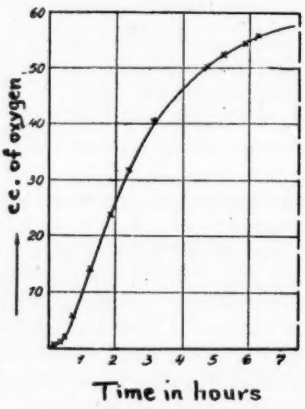

Figure 3

water again condenses in the cooler capillary and in the burette, and in this way causes a subsequent slight diminution in the volume of gas. This is obviously the case also with the oxygen curve.

TABLE I

Time in Hours and Minutes	Trend of the Oxygen Curve	Trend of the Nitrogen Curve	Course of the Reaction, *i. e.*, Quantity in Cc. of Oxygen Absorbed
0 00	0.0	0.0	0.0
10	−31.0	−32.7	0.8
20	−32.2	−33.8	1.6
30	−31.6	−33.9	2.3
45	−27.5	−33.7	6.2
1 15	−19.0	−33.5	14.5
50	− 8.6	−32.6	24.0
2 25	− 0.2	−32.1	31.8
3 10	8.6	−32.2	40.8
4 45	18.5	−32.0	50.5
5 15	20.6	−31.9	52.5
55	22.4	−32.3	54.7
6 15	23.9	−32.0	55.9

Our films behaved in a similar way, as will now be shown. Accordingly, the nitrogen curve can be used safely as a control or reference system for the oxygen curve. The values obtained for the results of the oxidation are shown in column 3 of Table I and by a curve such as that in Fig. 3.

The successful way in which the experiments were repeated is seen in Fig. 4, which represents a one cubic centimeter film of latex and four cubic centimeters of a 10-millimolar copper sulfate solution. Curves I to IV represent four independent series of measurements; Curve V gives the average of them all. The deviations in the individual values from the mean do not in general exceed ±5 per cent. It may be well to point out in this connection that in experiments lasting for a long time, such as those with antioxidants, the individual series of measurements varied up to ±10 per cent from the average value and at times much more, so that individual measurements which deviate abnormally had to be discarded. The values given in the following tables and curves are the average of at least three experiments.

It was still necessary to study the influence of the time of drying on the course

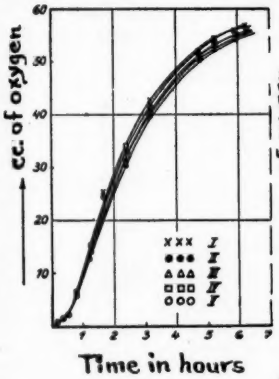

Figure 4

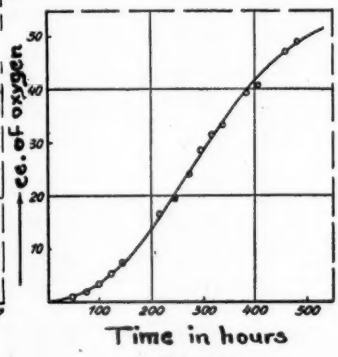

Figure 5

of the reaction. It was found that drying of the film was complete after only twenty-four hours, and it could be left longer in the vacuum desiccator without influence on the normal course of oxidation. Here too the measurements were made on films prepared from one cubic centimeter of latex and four cubic centimeters of a 10-millimolar copper sulfate solution. These were dried for different times, *viz.*, 24, 48, 72, and 96 hours, respectively, before the rate of oxidation was measured. The curves obtained fall practically within the limits of error.

II. Experimental Results

(a) **Influence of Catalysts.**—In the first place, the rate of oxidation of ordinary ammonia-treated latex was studied. Table II and Fig. 5 show the course of the reaction for one cubic centimeter of 18.01 per cent latex.

Special attention was paid to the influence of various catalytically active heavy metal salts on the rate of oxidation of pure latex.[9] Of the salts studied only the results for copper sulfate, manganese sulfate, cobalt nitrate, and iron chloride are given in Table III. Values were obtained for films prepared from one cubic centimeter of latex and four cubic centimeters of the 10-millimolar salt solution.

The influence of the concentration on the rate of oxidation was studied with two of these salts, *viz.*, copper sulfate and manganese sulfate. The films were

TABLE II

Time in Hours and Minutes	Quantity of Oxygen Absorbed in Cc.
0 00	0.0
48 00	0.9
74 15	2.2
97 30	3.6
122 00	5.5
143 00	7.6
215 00	16.6
242 00	19.8
271 30	24.3
295 20	28.9
314 30	31.5
337 10	33.4
383 30	39.7
406 50	41.2
458 10	47.8
480 30	49.2

TABLE III

Quantity in Cc. of Oxygen Absorbed per 1 Cc. of Latex and 4 Cc. of a 10-Millimolar Solution of

Time in Hours and Minutes	Copper Sulfate	Manganese Sulfate	Iron Chloride	Cobalt Nitrate
0 00	0.0	0.0	0.0	0.0
10	0.8			
20	1.6	1.6		3.8
30	2.3	4.0	0.2	5.7
45	5.8	8.0	2.3	9.3
1 00			7.1	13.3
15	14.4	15.1	13.1	18.1
30			20.2	22.5
50	24.4	22.9		
2 00			28.6	29.5
25	32.4	28.3		
30			34.7	36.8
50			37.8	40.2
3 10	41.8	34.7		
4 30			49.1	46.9
45	51.3	43.8		
5 15	53.4	48.1		
30			53.4	49.7
55	55.3			
6 05			55.6	50.3
15	56.4			
30		54.0		
40			57.5	

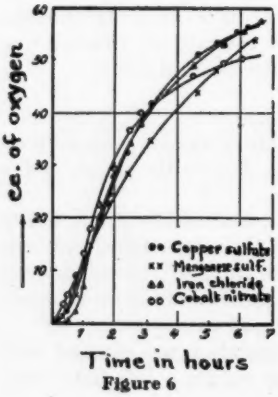

Figure 6

prepared in the usual way, though the concentration of the salt was varied as follows: copper sulfate, 0.1, 0.5, 1, 5, 10, and 100 millimols per liter; manganese sulfate, 0.5, 1, 5, 10, and 100 millimols per liter. This corresponds in the case of copper sulfate to approximately 0.014, 0.07, 0.14, 0.7, 1.4, and 14 per cent copper, and for manganese sulfate to approximately 0.06, 0.12, 0.6, 1.2, and 12 per cent manganese, calculated on the dried latex substance.

The results are shown in Tables IV and V. Figure 7 gives the values obtained with manganese sulfate, which are typical.

It is seen that the rate of oxidation depends preponderantly upon the concentration of the heavy

TABLE IV

Quantity of Oxygen Absorbed per 1 Cc. of Latex and 4 Cc. of a Copper Sulfate Solution of a Concentration per Liter of

Time in Hours and Minutes	0.1 m-Mol.	0.5 m-Mol.	1 m-Mol.	5 m-Mol.	10 m-Mol.	100 m-Mol
0 00	0.0	0.0	0.0	0.0	0.0	0.0
20					1.8	
30					2.3	0.8
40					4.7	
45					5.8	
1 00			0.3	4.0		6.5
15					14.4	
20				8.8		
30			1.5			13.5
50				16.9	24.9	
2 00			3.2			
10				22.9		
25					32.4	
30						33.8
50				31.5		
3 10			10.0		41.8	
20				36.4		
25						49.2
4 00				40.5		
45					51.3	
50				46.0		
55						60.6
5 00			27.8			
15					53.4	
50				49.3		
55					55.3	64.4
6 15			39.9		56.4	
40		0.4		51.4		
7 00			45.7			
55			51.0			
23 30		42.4				
24 20		46.9				
25 00		49.6				
26 10		53.2				
30	3.5					
45		54.3				
27 30		56.2				
29 10		59.5				
40		60.3				
30 00	5.1	61.0				
71 10	37.9					
79 25	44.5					
95 30	59.7					
101 00	63.2					
102 40	64.0					
103 10	64.3					

metal salt; in fact as little as 0.014 per cent of copper and 0.06 per cent of manganese are sufficient to bring about very rapid destruction of the rubber latex. These values agree very well with those of C. O. Weber[10] and Kirchhof,[11] who used commercial rubber.

With increasing concentrations of salt, the rate of oxidation increased from that of pure latex to an optimum, which remained the same over a certain range of concentrations. Upon passing to still higher concentrations of the heavy metal salt, there was a distinct drop in the rate of oxidation. The rate of oxidation of films containing copper sulfate and manganese sulfate solutions in 100-millimolar concentration showed this tendency to diminish. Here the rate of oxidation at the

TABLE V

Time in Hours and Minutes	Quantity of Oxygen Absorbed for 1 Cc. Latex and 4 Cc. of a Manganese Sulfate Solution with a Concentration per Liter of 0.5 *m*-Mol.	1 *m*-Mol.	5 *m*-Mol.	10 *m*-Mol.	100 *m*-Mol.
0 00	0.0	0.0	0.0	0.0	0.0
20				1.6	
30				4.0	
35			1.1		2.1
45				8.0	
50			2.5		4.2
1 10			4.6		
15				15.1	
20					16.6
45			9.0		
50				22.9	
2 05			11.0		
20					31.9
25				28.3	
35			14.1		
50					41.0
3 10				34.7	
15		0.2	18.0		
25					47.5
4 35	0.8				
45				43.8	
50					56.4
5 05			27.6		
15				48.1	
35			30.7		58.1
40		3.3			
6 20					61.5
30				54.0	
35			36.4		
45	2.3				
50		5.1			63.0
7 30		5.7	51.8		
8 55		8.9			
22 50	28.1				
23 30		48.3			
24 05	32.4				
25 05		51.2			
26 40	36.0				
27 20		54.9			
29 05	41.2				
55		58.6			
30 15	43.6				
45		60.0			
35 10		63.2			
47 00	65.1				

beginning of the reaction was lower than that of a film to which only a 10-millimolar solution of the corresponding salt had been added, though naturally the rate of oxidation in the later stages became greater with the concentrated solutions. When still higher concentrations of salt were used, *e. g.*, 500-millimolar solutions, the films not only did not show an increased rate of oxidation, but there was a distinctly slower absorption of oxygen than with films from latex containing no heavy metal salts. Here the heavy metal salt acts as a protective agent, a phenomenon which is not easily explained. It might possibly be that after the film is dried, a layer of copper salt is formed, which prevents oxygen from entering the film and in this way retards oxidation. If the films had not been so extremely

thin in the beginning, it might be reasonable to assume that there was a change in the surface layer from rapid oxidation.

In this connection Williams[12] observed that when he painted vulcanized rubber films with an alcoholic solution of a copper salt and allowed ozone to act upon them, the films deteriorated more slowly than similar films which had not been so

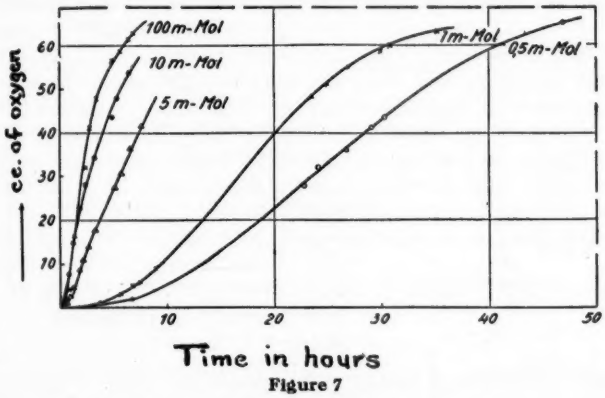

Figure 7

treated. He attributed this phenomenon to the fact that in the presence of the heavy metal salt the surface became soft very rapidly under the influence of ozone, and that the surface layer thus formed, prevented mechanically the further entrance of ozone into the deeper-lying rubber particles.[13]

The results of Thomson and Lewis and also those of Kirchhof on the action of individual salts were confirmed.[14] Above a certain concentration, cobalt and manganese salts are more active than copper salts (see Table III and Fig. 6), which is not the case with lower concentrations of these salts. This has also been observed by Kirchhof in the case of manganese. He showed that under certain conditions manganese salts, especially in the presence of iron salts, are more active than copper salts.

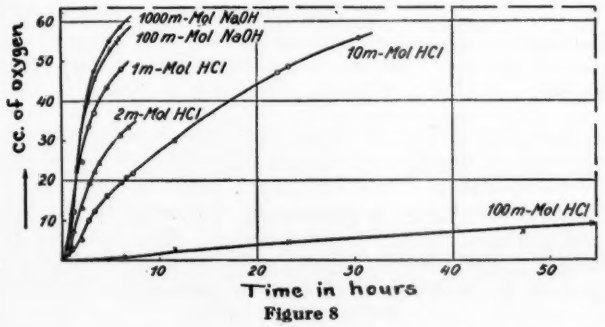

Figure 8

(b) **The Influence of p_H.**—It is well known that the rate of autoöxidation processes depends greatly on the p_H value. It was therefore necessary to ascertain whether the autoöxidation of rubber latex is also influenced by its acidity or alkalinity. With this in view, films were prepared from mixtures of one cubic centimeter of latex and four cubic centimeters of a 10-millimolar copper sulfate

solution containing on the one hand two cubic centimeters of 1000 and 100-millimolar sodium hydroxide, and on the other hand with 1, 2, 10, etc., to 100-millimolar hydrochloric acid solution. Figure 8 gives the results,[15] which show that the autoöxidation of rubber latex is greatly retarded by the addition of acids and is accelerated by alkalies.

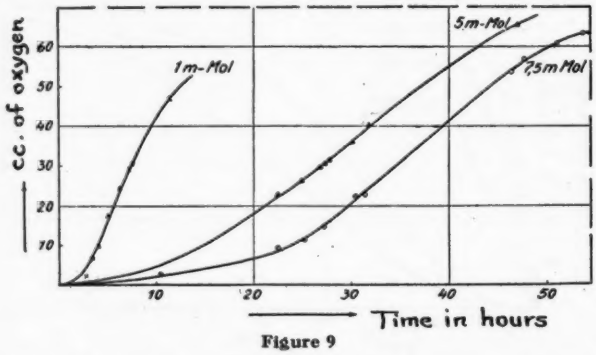

Figure 9

The potential alkalinity or acidity as well as the p_H values of the mixtures used to prepare the films were tested. The method first used was that of Hauser and Scholz,[16] and the alkalinity of the solution was determined titrimetrically with phenolphthalein as indicator. The p_H was then measured by the aid of a Wulff foil colorimeter.[17] With respect to the difficulties, especially the precision of the measurements, one is referred to the work mentioned and to an investigation by Mackay.[18]

The values given in Table VI do not represent absolute values, but give only a relative picture of the conditions of the experiment; the measurements are not those of the dried films ready for the oxidation but are those of the corresponding freshly prepared solutions.

TABLE VI

	1 Cc. of Latex + 4 Cc. of a 10-Millimolar Copper Sulfate Solution + 2 Cc. of						
	1000 *m*-Mol. NaOH	100 *m*-Mol. NaOH	Without NaOH and HCl	1 *m*-Mol. HCl	2 *m*-Mol. HCl	10 *m*-Mol. HCl	100 *m*-Mol. HCl
Potential alkalinity or acidity in cc. 0.1 *N* acid or alkali	19.5 HCl	1.55 HCl	0.45 NaOH	0.48 NaOH	0.50 NaOH	0.65 NaOH	2.45 NaOH
pH....	11.4	10.4	7.3	6.8	6.8	6.7	4.2

In contrast to the phenomena found in certain other autoöxidations, *e. g.*, that of sulfite in the presence of cupric ions, which is inhibited both in acid and in alkaline solutions, the autoöxidation of rubber latex is inhibited only in acid solution. In alkaline medium it is highly accelerated by decreasing the hydrogen-ion concentration, and increases steadily to an optimum. The fact that the oxidation is greatly retarded in acid medium appears to be at variance with the observation that acids promote the tackiness of rubber,[19] a phenomenon which is attributed to oxidation.

On the other hand, in the more highly alkaline samples it appears that the rubber is changed by the action of alkalies, so that it is more rapidly oxidized. In any case, with 10-millimolar copper sulfate solution and 1-millimolar sodium hydroxide solution, the length of the time of drying of the films seemed to exert an influence, in the sense that the films which were dried for a longer time oxidized somewhat more rapidly at first.

(c) **The Influence of Inhibitors.**—In conclusion a few substances were studied which usually have a retarding influence on autoöxidation,[20] namely, the three homologues, pyrocatechol, resorcinol, and hydroquinone, as well as hexamethylenetetramine, which is used in the rubber industry as an accelerator. In this connection it should be mentioned that mannite, which distinctly retards[21] the catalytic effect of copper ions in the autoöxidation of sulfite, has no significant influence on the autoöxidation of rubber latex.

The experiments were carried out with films which were prepared from one cubic centimeter of latex, four cubic centimeters of a 10-millimolar copper sulfate or manganese sulfate solution, and two cubic centimeters of a solution of antioxidants. As antioxidants, pyrocatechol, hydroquinone, resorcinol, and hexamethylenetetramine were studied at various concentrations. Figures 9 and 10 give typical results of measurements of films prepared from highly active pyrocatechol to the least active hexamethylenetetramine, in both cases with copper sulfate as catalyst. Hydroquinone and resorcinol have an intermediate activity, and more nearly resemble pyrocatechol.

The same result was obtained when manganese sulfate was used in place of copper sulfate. The values for these measurements are accordingly omitted here. However it should be mentioned that the retarding effect of the individual substance on manganese sulfate was more pronounced than on copper sulfate. Thus, the autoöxidation of films prepared from one cubic centimeter of latex and four cubic centimeters of a 10-millimolar manganese sulfate solution by the addition of two cubic centimeters of a pyrocatechol solution was retarded to such an extent that it was hardly greater than the autoöxidation of the latex films without any addition.

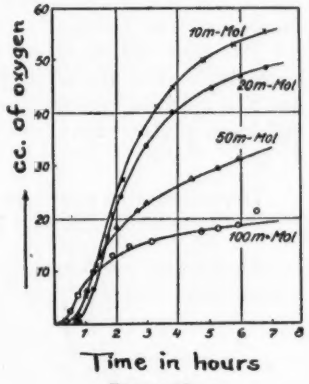

Figure 10

This phenomenon is of great importance since it is evidently possible to prevent or in any case to retard considerably the deterioration of rubber, which is often observed in practice due to heavy metals and their salts, by the addition of antioxidants or protective agents. In this connection attention should be called to an investigation by Bierer and Davis,[22] who observed that certain common protective agents used in practice retard the destruction of rubber by copper salts. Similar results were also obtained by Jones and Craig,[23] who recommend the addition of antioxidants to mixtures containing copper or to mixtures which come in contact with copper armatures in order to give greater protection against aging to the rubber products.

So far little attention has been paid to these investigations, which are of fundamental importance for the protection of rubber, and therefore particular emphasis is laid at this moment upon their far-reaching practical importance.

III. General Part

The fact that the autoöxidation of rubber, like so many autoöxidation phenomena, is autocatalytic, was first pointed out by Wo. Ostwald[24] and soon afterward by Kirchhof.[25] Accordingly it has an S-shaped curve, with a very low initial velocity during the induction period and a subsequent sharp rise. As in many other cases, the trend of the curve may be expressed by the autocatalytic reaction equation of the first order of Wm. Ostwald.[26]

$$\frac{dx}{dt} = k(a - x)(b + x) \tag{1}$$

or, in integrated form:

$$k = \frac{1}{t(a + b)} \log \frac{b + x}{a - x} \tag{2}$$

where x is the quantity of oxygen absorbed in time t, a the maximum quantity absorbed, k a constant, and b a value which is derived from the equation:

$$b = a - 2x_m \tag{3}$$

where in turn x_m is the value of x at the inflection point of the curve. The validity of this relation will not be discussed further here. For one thing the constancy of the k value was only fairly good. It may appear questionable then whether the curve really represents a simple phenomenon. It might very well be that some other autoöxidizable substances present in the latex were rapidly oxidized in the beginning, and that in the oxidized form they were the actual autocatalysts and accordingly governed the induction period.[27]

It should be noted that with the aid of constant k obtained from Equation 2, the dependence of the relation of the rate upon the concentration of the positive catalyst can be obtained. Table VII shows this for copper sulfate and gives the average k values. It is seen that the rate increases sharply for intermediate concentrations of the salts, decreases somewhat for high concentrations, and at low concentrations gradually approaches the value found for latex to which heavy metal salt solutions have not been purposely added.

TABLE VII

DEPENDENCE OF THE ACTIVITY OF COPPER SULFATE ON THE CONCENTRATION

Concentration in Millimols per Liter	k
0.0	0.00014
0.1	0.00073
0.5	0.0026
1.0	0.0073
5.0	0.015
10.0	0.020
100.0	0.017

In other respects, too, the autoöxidation of latex is similar to other autoöxidation processes, such as the positive catalytic effect of heavy metal salt solutions, the antioxygenic effect of many organic substances, and the formation of hydrogen peroxide.[28] The autoöxidation of latex, as Wo. Ostwald has already pointed out,[29] is surprisingly similar to that of linseed oil[30] especially in the way they behave experimentally. Recently considerably more light has been thrown on the mechanism of such reactions as the autoöxidation of sulfite under the catalytic influence of cupric ions, and of ultra-violet light. The phenomenon represents a chain reaction, in which a very reactive radical, monothionic acid, occurs as an intermediate product.[31] However, so far as we can see, our measurements lead to no far-reaching conclusions. Perhaps an investigation of the accelerating effect of light would have assisted us more, but unfortunately this was not possible to carry out. This has already been studied many times in the case of commercial rubber,[32] and probably it is true that rubber latex would behave in a similar way in all essential respects. However, in order to be able to draw any further conclusions, such measurements would have to be strictly comparable to ours, and among other things the influence of the p_H value on the light reaction would have to be known; results which are still lacking.

Perhaps in making a comparison with other autoöxidation processes it might be well to consider that peculiarities in the behavior of rubber latex may be caused by oxidation on the surface of the rubber particles, so that a heterogeneous system is involved, not a homogeneous one, as in the case of the sulfite mentioned above.

Summary

1. The absorption of oxygen by rubber latex was studied in its relation to the time, and the quantity of oxygen used was determined volumetrically.

2. Among the substances which are positive catalysts in these reactions, the salts of a few heavy metals, copper, manganese, iron, and cobalt were investigated. The effect of the concentration was also studied in the case of copper and manganese. At medium concentrations the rate increased greatly, at high concentrations it diminished, and at very low concentrations it gradually approached the value for rubber latex to which no heavy metal salt solution had been added.

3. The retarding effect of antioxidants was studied with the aid of pyrocatechol, hydroquinone, resorcinol, and hexamethylenetetramine, in the presence of copper or manganese as positive catalysts. Pyrocatechol was the most active, and hexamethylenetetramine was very much less active than the three just mentioned.

4. In the presence of copper as positive catalyst, the rate of oxidation in its relation to the p_H value was measured. In strongly acid medium the rate was relatively low, while it increased with increase in alkalinity, and when the medium became strongly alkaline it reached high values which no longer increased markedly.

5. The autoöxidation of rubber latex as a function of the time can be satisfactorily expressed in all cases in an approximate way by the autocatalytic equation of the first order:

$$\frac{dx}{dt} = k(a - x)(b + x)$$

where x is the quantity of oxygen absorbed in time t, a the maximum quantity of oxygen absorbed, k the velocity constant, and b a value which depends upon a and x_m, the latter the x value at the point of inflection.

References

[1] Peachey, *J. Soc. Chem. Ind.*, **31**, 1103 (1912); Peachey and Leon, *Ibid.*, **37**, 55 (1918); Leon and Lister, *Ibid.*, **46**, 220 (1927); Kohman, *J. phys. Chem.*, **33**, 226 (1929).

[2] Morgan, *The Preparation of Plantation Rubber*, 2nd Ed., London **1914**, pages 161–166; van Rossem and Dekker, *Ind. Eng. Chem.*, **18**, 1152 (1926); Martin, *Trans. Inst. Rubber Ind.*, **2**, 354 (1926–27).

[3] van Rossem and Dekker, *Loc. cit.*, note 2.

[4] See note 1.

[5] Peachey and Leon, *Loc. cit.*, note 1; Mead and Pope, *India Rubber World*, **73**, 326 (1926).

[6] Kohman, *Loc. cit.*, note 1.

[7] *Ind. Eng. Chem.*, **22**, 874 (1930).

[8] *Biochem. Zeitschrift*, **100**, 230 (1919).

[9] For the catalytic action of salts of heavy metals on the oxidation of commercial rubber, see Thomson and Lewis, *Chem. News*, **64**, 169 (1891); C. O. Weber, *J. Soc. Chem. Ind.*, **9**, 546 (1900); Kirchhof, *Kautschuk*, **3**, 239, 256 (1927); **7**, 26 (1931).

[10] See note 9.

[11] See note 9.

[12] *Ind. Eng. Chem.*, **18**, 367 (1926).

[13] This process is said to have been used on a practical scale in the U. S. (see van Rossem, *Die amerikanische Gummi-Industrie und ihre wissenschaftliche Arbeit*, Berlin, **1928**, p. 54).

[14] Contrary to the results of Thomson and Lewis we found that iron is a positive catalyst, which has also been found by others.

[15] It should be mentioned that the experiment with 100-millimolar hydrochloric acid was carried out for 119 hours; the rise remained practically linear and reached a value of 22.6 cc.; at the end of 54 hours it had reached the value of 9.3.

[16] *Kautschuk*, **3**, 304 (1927).

[17] *Kolloid-Z.*, **40**, 341 (1926).

[18] *India Rubber J.*, **79**, 353 (1930).

[19] Eaton and Day, *J. Soc. Chem. Ind.*, **38**, 339 (1919); Spence, *Kolloid-Z.*, **4**, 75 (1909); Fickendey, *Ibid.*, **9**, 81 (1911).

[20] For the action of such antioxidants on rubber, see Naunton, *Trans. Inst Rubber Ind.*, **5**, 442 (1929).

[21] Bigelow, *Z. physik. Chem.*, **26**, 493 (1898); Titoff, *Ibid.*, **45**, 641 (1903).

[22] *Trans. Inst. Rubber Ind.*, **3**, 151 (1927–28).

[23] *Ind. Eng. Chem.*, **23**, 23 (1931).

[24] Cf. Peachey, *J. Soc. Chem. Ind.*, **32**, 179 (1913).

[25] *Kolloid-Z.*, **13**, 49 (1913).

[26] *Lehrbuch d. allgem. Chem.*, Vol. II, 2, p. 264.

[27] See van Rossem and Dekker, *Loc. cit.*, note 2.

[28] See Kirchhof, *Loc. cit.*, under note 25; Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).

[29] *Loc. cit.*, note 24.

[30] This has been studied especially by Genthe (*Z. angew. Chem.*, **19**, 2087 (1906). The parallelism is so close that Stern and Puffett (*Trans. Inst. Rubber Ind.*, **8**, 216 (1932–33) have carried out an experiment in order to test the activity of the antioxidants and protective agents against aging used in the rubber industry from the point of their influence on the drying of linseed oil.

[31] Baeckstroem, *J. Am. Chem. Soc.*, **49**, 1460 (1927); Haber, *Naturwissenschaften*, **19**, 450 (1931); Haber and Franck, *Sitzungsber. Preuss. Akad. Wissensch., physik-mathem.*, Kl., **1931**, 250; Graf Schweinitz, *Ueber die Autoxydation des Sulfits, usw. Dissertation*, Berlin, **1927**.

[32] Kirchhof, *Loc. cit.*, note 9; Henry, *Caoutchouc et gutta-percha*, **7**, 4371 (1910); Asano, *India Rubber J.*, **70**, 307, 347, 389 (1925); Yamasaki, *J. Soc. Chem. Japan*, **29**, 1 (1927); Williams, *Loc. cit.*, note 12; Jecusco, *Ind. Eng. Chem.*, **18**, 420 (1926).

[Translated for Rubber Chemistry and Technology from Kautschuk, Vol. 9, No. 5, pages 70–72 May, 1933.]

Rubber Antioxygens

III. The Behavior of Natural and Artificial Protective Agents toward Sunlight and Ultra-violet Light (Preliminary Communication)

F. Kirchhof

HARBURG-WEG.

The destructive effect of sunlight and of artificial kinds of light on rubber has been known for a long time, without the cause being fully understood. It has also been known that the extent of the destruction depends to a great degree upon the presence or absence of natural or artificial protective agents, though the part played by antioxygens in protecting rubber from light has likewise not been fully explained.[1]

The aim of the present work is to call particular attention, on the one hand, to a

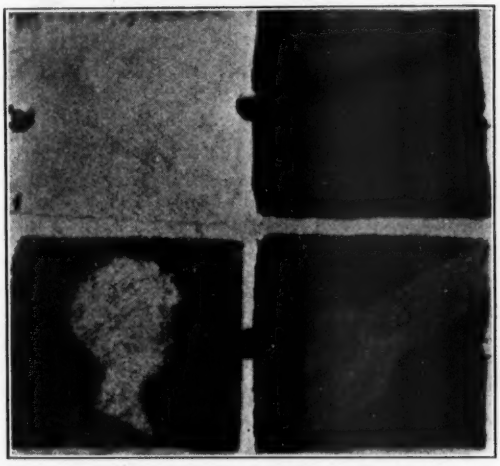

Figure 1

1. Untreated film of light Ceylon crepe (III).
2. The same after 10 hours' development with silver solution.
3. Development after 12 hours' exposure of the "head" to sunlight.
4. The same after 10 hours' exposure of the light part with ultra-violet light.

few simple experiments on the effect of light (sunlight and ultra-violet light) on raw rubber, and, on the other hand, to devise a simple method with which the effect of light on rubber can be detected quickly and with certainty.

In order to do this, advantage was taken of the property of natural water-soluble substances in raw rubber of reducing ammoniacal silver nitrate solution even at ordinary temperature. Since these reducing substances doubtless play an essential part in the protective action during aging, this property can be considered characteristic of certain groups of natural protective agents. Thus the particularly

high reducing power of the water extract of smoked sheet is doubtless to be attributed to substances from the smoke (cresols), while with crepes the reducing sugars may be chiefly responsible.

In the case of light-colored crepes, this reducing action of the extracted substances can be shown very well directly on the rubber if a sheet of pale crepe (Grade III) which has not previously been exposed for any great length of time to direct sunlight is immersed for a few hours in a ten per cent weakly ammoniacal silver nitrate solution.[2] After only a few hours a distinct brown color appears, and after eight to ten hours an intense gray to black color, as a result of the deposition of metallic silver. The silver is precipitated in the rubber in the finest state so that the treated samples give the impression of rubber films containing carbon black (Figs. 1 and 2). A sheet of extracted crepe does not have this appearance; so that this appearance is accordingly dependent upon the presence of reducing extractable substances.

Figure 2—Effect of Sunlight on the Most Highly Purified Tjipetir Gutta-Percha. The Darkening of the Exposed Surface (Head) Appears Only after Development with Silver Solution.

Sheets of pale crepe which are treated, as is known, with a bleaching agent (sodium sulfite) do not show any reduction of the silver solution. On the contrary, strips of smoked sheet have a very marked reducing action.

It remained to be considered whether light in conjunction with oxygen would bring about destruction of these reducing substances, and in this way destroy their protective action. According to this, crepe rubber exposed to light for a rather long time would lose its ability to reduce ammoniacal silver nitrate solution.

A simple experiment to ascertain this confirmed the correctness of this idea. A paper pattern with a design cut out was laid on a sheet of the crepe rubber mentioned above, and the whole thing was exposed in a printing frame to sunlight for three periods of four hours each. The sheet of crepe was then left in ammoniacal silver nitrate solution for eight hours, washed thoroughly and then dried. The effect of light and of the subsequent "development" is distinctly seen in Picture 3 of Fig. 1. The exposed surface lost its ability to reduce the silver solution, and

therefore remained pale during the treatment, whereas the untreated surface turned black, as is evident in Picture 2 of Fig. 1.

It is of further interest that the upper surface of the film exposed to sunlight was somewhat lighter before "developing" than the covered surface, so that sunlight at least during the first stage of the reaction exerted a distinctly "bleaching" effect on certain colored substances in the rubber. The destruction of the reducing protective substances runs parallel with this bleaching action, probably because the same agent is responsible.[3]

As far as the destruction of the reducing substances is concerned, ultra-violet light behaves in exactly the same way. Figure 1, Picture 4, shows the effect after two hours' exposure of the same kind of pale crepe (Grade III) with a quartz-mercury 220 v., 2 amp. load at 30 centimeters distance. Here, too, there was almost no reducing effect on the illuminated part, and therefore it remained light during the development with silver nitrate.

In contrast to the action of sunlight, the upper surfaces of the crepe irradiated with ultra-violet light for a longer time (about two hours) became distinctly yellow, probably because of the formation of colored oxidation products of the rubber, *viz.*, peroxides. This peroxide formation also appears to explain why the surfaces irradiated with ultra-violet light were not so light after the development as those exposed to sunlight, since these traces of peroxides themselves reduce ammoniacal silver nitrate solution.

This supposition was confirmed by the behavior of the most highly purified Tjipetir-gutta-percha exposed to sunlight or ultra-violet light. A freshly cut surface or a snow-white film from this hydrocarbon obtained from solution turned yellow at the irradiated places after rather long exposure, regardless of whether sunlight or the quartz lamp was used.

Figure 3

1. Light ceylon crepe (Grade III) after exposure to ultra-violet light in stages. The left darker strip was exposed about 5 minutes.
2. Pale crepe exposed and developed for the same length of time.
3. Strips of pale crepe impregnated with 1 per cent solutions of different antioxidants. The lower halves were exposed to ultra-violet light 2 hours and developed. Hy = hydroquinone, Pa = parazone, Ph = phenyl-β-naphthylamine, M. B. = "M. B."

In the case of the ultra-violet light, a change in the irradiated places was noted after only a brief exposure, even before the appearance of a yellowish color. Examined obliquely to the light these areas appeared more or less highly glazed, in contrast to the dull protected parts of the film. When such a partially irradiated film was put into an ammoniacal silver nitrate solution, the exposed place turned brown in contrast to the crepe rubber film treated in the same way, whereas the unexposed part remained pure white because of the lack of reducing protective substances (see Fig. 2).[4]

The browning of the irradiated places is doubtless to be attributed to the formation of reducing peroxides of the gutta-percha hydrocarbon. The well-known marked sensitivity to light of pure, unprotected gutta-percha agrees with this observation.[5]

A few experiments on the extent of this sensitivity of reducing protective substances toward ultra-violet light were carried out. A strip of Ceylon pale crepe (Grade III) was exposed in sections every five minutes to the ultra-violet light already described, and was then developed (Fig. 3, Picture 1). The left (dark) part of the sheet which was irradiated for five minutes still showed a strong reducing action, when it was developed. After an exposure of twenty minutes a distinct diminution in this effect was noticeable. After two hours' exposure to ultra-violet light the reducing power of the natural protective agents completely disappeared to a depth of one millimeter (Fig. 3, Picture 2). After about four hours' exposure to sunlight a distinct diminution of the reducing action occurred.

Finally the behavior of a few artificial protective agents toward the action of ultra-violet light was studied. To this end, strips of pale crepe which, as mentioned above, showed no reducing action, were immersed in one per cent benzene solutions of hydroquinone, "Parazone" (du Pont) and phenyl-β-naphthylamine ("Age-Rite powder") for ten seconds and in an acetone solution (because of its difficult solubility in benzene) of the protective agent "M. B." (I. G. Farbenindustrie) for sixty seconds, were dried in darkness, and then the lower halves were exposed for two hours to the quartz lamp under the conditions described above. After this exposure, only the irradiated portion of the strip impregnated with phenyl-β-naphthylamine had become an intense yellow color, whereas the others showed almost no change. The strips irradiated in this way were then treated with ammoniacal silver nitrate solution. It was found that the impregnation with hydroquinone and "Parazone" and the two-hour irradiation with ultra-violet light had not impaired their reducing action at all, whereas strips treated with phenyl-β-naphthylamine and "M. B." showed no reducing action, even on the protected upper halves. The darker lower halves of these last mentioned strips are explained by the yellowing brought about by the formation, during exposure, of colored oxidation products of these protective agents, which underwent a certain darkening of color during the development.

Since hydroquinone and "Parazone" have a marked protective effect on rubber exposed to light, it appears that this protective effect is related to the reducing action of these substances. The fact that the latter are relatively unaffected by long exposure to light explains their continued protective action at relatively low concentrations.

The method described here seems to be suitable for evaluating and obtaining quantitative data upon protective agents against aging, at least for those the protective action of which depends upon their reducing power.

Summary

It has been shown that the reducing power of the water-soluble substances extracted from raw rubber is destroyed by the action of sunlight and ultra-violet light on raw rubber. This effect of light may be seen in a very striking way by treatment with an ammoniacal solution of silver nitrate of partially irradiated rubber sheets, which in a certain sense represents a "development."

In contrast to raw rubber, the most highly purified Tjipetir-gutta-percha, which contains no protective substances sensitive to light, forms peroxides with natural or artificial irradiation. These peroxides in turn reduce ammoniacal silver nitrate solution, so that irradiated samples of crepe rubber and Tjipetir-gutta-

percha when developed with the reagent mentioned give pictures which behave negatively and positively.

Finally the behavior toward ultra-violet light of a few artificial protective agents was investigated.

Further experiments will be devoted to the problem of vulcanized rubber under the same conditions.

References

[1] See also the excellent work: "The Autoöxidation of Rubber Latex," by Freundlich and Talalay, *Kautschuk*, **9**, Nos. 3 and 4 (1933).

[2] This solution is obtained when an approximately ten per cent solution of silver nitrate is added dropwise to concentrated ammonia until the original precipitate of silver hydroxide just disappears.

[3] It does not appear to be entirely certain whether this agent is hydrogen peroxide, which reduces silver solution itself (Russell effect). A crepe film, on which letters were drawn with hydrogen peroxide, showed after a few minutes' exposure and subsequent washing with water, much greater darkening than the rest of the surface after development. It may be possible that in the action of light on rubber, hydrogen peroxide forms at first only within the mass because reducing protective substances are present, so that it cannot form in excess or even occur at all until the rubber hydrocarbon begins to autoöxidize itself.

[4] The peculiar graining of the gutta-percha film is a result of the formation of a network structure during evaporation of the solution. This network structure grows over the surface in a leaf vein-like manner. These "nets" form centers for the further progress of crystallization within the film. The phenomenon is therefore analogous to the ice flower formation in the case of other crystallizing substances.

[5] Kirchhof, *Kautschuk*, **4**, 254 (1928).

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Studies on the Nature of the Action of Organic Accelerators for Rubber Vulcanization

II. Special Properties of Organic Accelerators. Part 1

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In previous communications the author has studied the effect of various organic accelerators on rubber sols, and has been led to the conclusion that organic accelerators can be classified into three main groups according to the characteristic manner

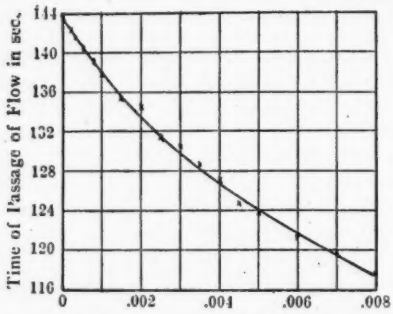

Figure 1—Mercaptobenzothiazole

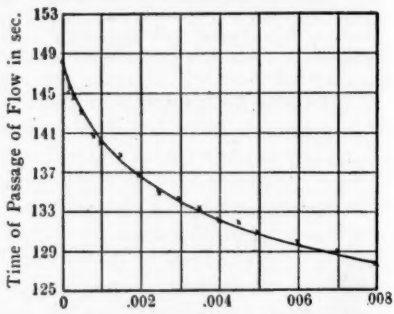

Figure 2—Tetramethylthiuram Monosulfide

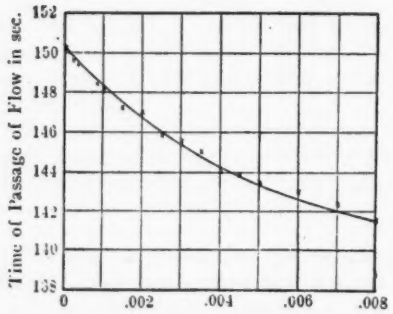

Figure 3—Nitrosobenzene

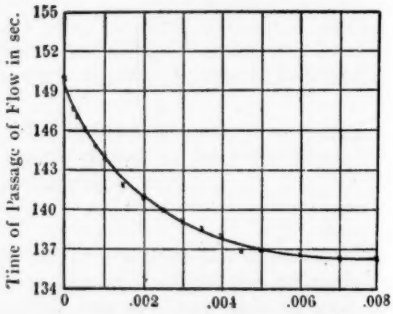

Figure 4—Dinitrophenyldimethyldithiocarbamate

in which they affect the viscosity of rubber solutions. The object of the present paper is to invite more quantitative considerations and discussion based on the

experimental results obtained in the previous papers. In the first part of this work the author has taken into consideration the special properties of the third group accelerators, which seem to be most important and significant from both a physico-chemical and a technico-chemical point of view.

As was described in the previous report, the lowering of the viscosity of rubber solutions by the third group accelerators, instead of coming sharply to an end, continues over a long period of time. In further experiments it has been found that increasing amounts of the third group accelerators also produce a progressively increasing reduction in viscosity, as shown graphically in Figs. 1 to 4. In the light of these facts it must be quite reasonable to expect the third group accelerators to be very active depolymerizing agents for the rubber hydrocarbon. The author has previously studied the effect of heat on rubber solutions, which may be summarized as follows. The viscosity of a rubber solution shows a marked decrease when the temperature of the solution reaches a point above 70° C., where depolymerization is considered to occur. The change in viscosity by heating is irreversible. The rate of decrease in viscosity of a rubber solution can be expressed by the following formula:

$$\eta_{t_0} - \eta_t = k.\log t$$

where η_{t_0} is the viscosity of an unheated rubber solution at 20° C. and η_t is the same as η_{t_0} except that the rubber solution is given a preliminary heating for t minutes; k is called "depolymerization constant."

In the previous communications the author assumed that the action of the third group accelerators on rubber sols may cause depolymerization of rubber hydrocarbon for the reason that the time-viscosity curve representing the effect of heating rubber solutions is almost identical with that representing the influence of the third group accelerators. If this is the case, then an empirical formula analogous to that above should hold for the experimental results obtained for the third group accelerators:

$$\eta_{t_0} - \eta_t = k.\log t$$

in which η_{t_0} is the viscosity of a rubber solution without addition of accelerator and η_t is the same as η_{t_0} except that the rubber solution is allowed to stand for t minutes after the addition of accelerator. Using the data given for mercaptobenzothiazole, dibenzothiazole disulfide, tetramethylthiuram monosulfide, *p*-nitrosophenol, and nitrosobenzene, the author calculated the depolymerization constant k, and obtained the following results.

TABLE I

MERCAPTOBENZOTHIAZOLE

Time Elapsed in Minutes, t_m	Time of Passage of Flow in Seconds, η_{230}	k	Time Elapsed in Minutes, t_m	Time of Passage of Flow in Seconds, η_{230}	k
0	156.4	..	95	141.6	7.48
15	153.1	2.81	105	140.1	8.07
25	151.6	3.43	120	137.6	9.04
35	150.1	4.08	135	135.3	9.91
45	148.6	4.72	150	132.7	10.90
55	147.4	5.17	165	131.1	11.41
65	145.8	5.84	180	128.1	12.55
75	144.3	6.45	195	125.6	13.44
85	143.0	6.95	210	124.1	13.91

TABLE II

DIBENZOTHIAZOLE DISULFIDE

t_m	η_{230}	k	t_m	η_{230}	k
0	160.0	..	95	150.1	5.01
15	158.2	1.53	105	149.0	5.44
25	157.1	2.07	120	147.3	6.10
35	156.3	2.40	135	146.3	6.43
45	155.4	2.78	150	144.1	7.31
55	154.1	3.39	165	142.7	7.80
65	153.4	3.64	180	140.6	8.60
75	152.4	4.05	195	139.6	8.91
85	151.6	4.35	210	138.0	9.47

TABLE III

TETRAMETHYLTHIURAM MONOSULFIDE

t_m	η_{230}	k	t_m	η_{230}	k
0	156.0	..	95	143.5	6.32
15	152.8	2.72	105	142.0	6.93
25	151.6	3.15	120	140.8	7.31
35	150.2	3.76	135	140.0	7.51
45	149.0	4.23	150	137.9	8.32
55	148.2	4.48	165	136.1	8.98
65	146.5	5.24	180	134.5	9.53
75	145.8	5.44	195	133.0	10.04
85	144.8	5.81	210	131.6	10.51

TABLE IV

p-NITROSOPHENOL

t_m	η_{230}	k	t_m	η_{230}	k
0	150.3	..	120	146.5	1.83
15	148.6	1.45	135	146.3	1.88
25	148.2	1.50	150	146.0	1.98
45	147.7	1.57	180	145.7	2.04
55	147.5	1.60	195	145.5	2.10
85	147.0	1.71	210	145.3	2.15

TABLE V

NITROSOBENZENE

t_m	η_{230}	k	t_m	η_{230}	k
0	146.0	..	95	130.7	7.74
15	142.4	3.06	105	129.3	8.26
25	141.0	3.58	120	127.0	9.14
35	139.5	4.21	135	124.5	10.09
45	138.1	4.78	150	122.2	10.94
55	136.5	5.46	165	119.8	11.82
65	135.2	5.96	180	117.3	12.73
75	133.6	6.61	195	114.9	13.58
85	132.0	7.26	210	112.3	14.51

It is quite important to note that the value k, which should be constant, becomes larger with an increase of time t. By plotting k against t, a straight line is obtained, as shown in Figs. 5 to 9. The depolymerization constant k, therefore, should be expressed by the following equation:

$$k = a + bt$$

where a and b are constants depending upon the nature of accelerators. Considering the value of k as a linear function of the time in the case of the third group accelerators, the author assumed that these accelerators when added to rubber sols,

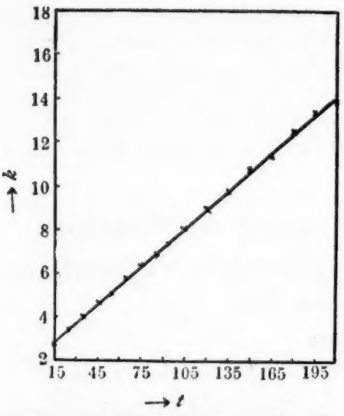

Figure 5—Mercaptobenzothiazole

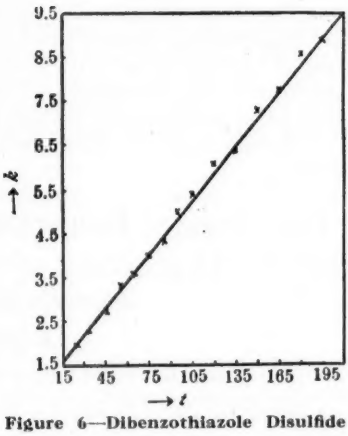

Figure 6—Dibenzothiazole Disulfide

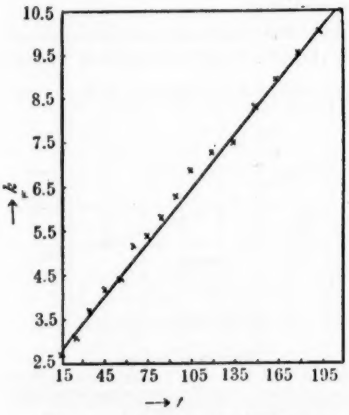

Figure 7—Tetramethylthiuram Monosulfide

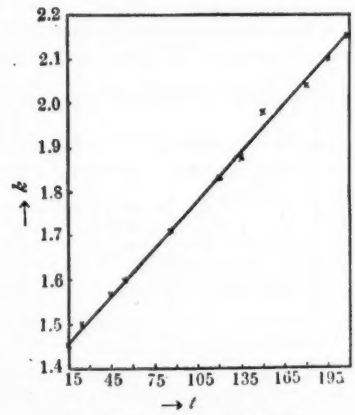

Figure 8—p-Nitrosophenol

not only depolymerize the rubber molecules, but also have some special effect on the rubber hydrocarbon. It has already been pointed out by Allessandri, Bruni and Geiger, Ostromislenski, Pummerer and Staudinger that the rubber hydrocarbon reacts with nitrosobenzene (which is included in the third group) in solution and forms isorubber nitrone. Judging from this fact, the author believes that the lowering effect on the viscosity of rubber sols of nitroso accelerators (except *p*-nitrosodimethylaniline as observed in the author's experiments) must be a result of depolymerization of the rubber and also a result of an attack on the double or molecular bonds of the rubber. In the opinion of the present

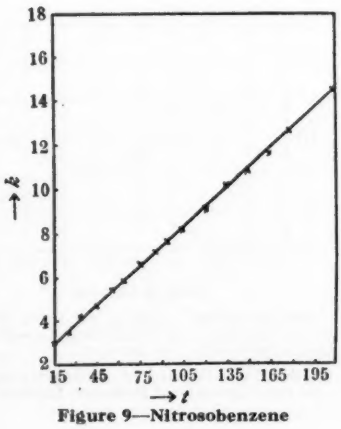

Figure 9—Nitrosobenzene

author, the effect of the third group accelerators on rubber sols is to be regarded as a combined action of breaking up of the rubber molecules and a chemical reaction of the depolymerized rubber with accelerators, and not to a break-down of micelles or aggregates, as is commonly believed. This new theory, advanced to account for the special properties of the third group accelerators, will be confirmed by further analytical-chemical experiments which are now in progress in the author's laboratory.

III. Special Properties of Organic Accelerators. Part 2. The Action of Ostromislenski's Vulcanizing Agents on Rubber Sols

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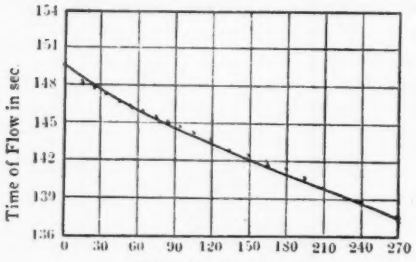
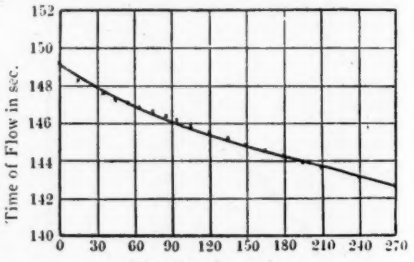
Continuing his previous studies, the author has carried out a number of experiments on the effect of Ostromislenski's so-called vulcanizing agents on the viscosity of rubber solutions. The work may be summarized thus:

1. The addition of small quantities of benzoyl peroxide, mono-, *m*-di-, and 1,3,5-trinitrobenzene to benzene-rubber sols causes a reduction in the solution viscosity



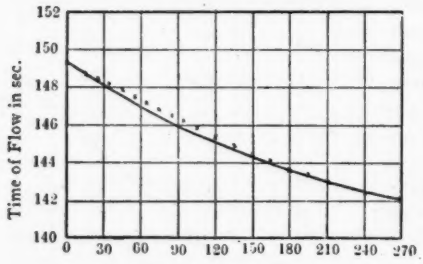
Amount added = 0.05 g. per 100 cc. of 0.4% rubber solution. (Acetone-extracted rubber used and benzoyl peroxide was added after dissolved in 1 cc. benzene.)

Figure 1—Influence of Benzoyl Peroxide on the Viscosity of Benzene-Rubber Sols



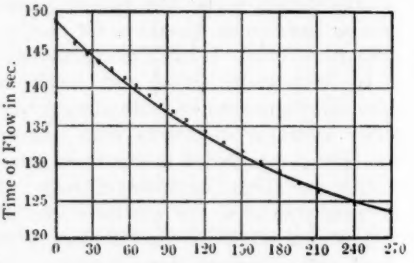
Amount added = 0.05 g. per 10 cc. of 0.4% rubber solution. (*m*-Nitrobenzene was added after dissolved in 1 cc. benzene.)

Figure 2—Influence of Nitrobenzene on the Viscosity of Benzene-Rubber Sols



Amount added = 0.05 g. per 10 cc. of 0.4% rubber solution. (*m*-Dinitrobenzene was added after dissolved in 1 cc. benzene.)

Figure 3—Influence of m-Dinitrobenzene on the Viscosity of Benzene-Rubber Sols

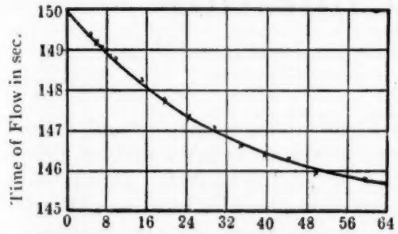


Amount added = 0.02 g. per 10 cc. of 0.4% rubber solution. (1,3,5-Trinitrobenzene was added after dissolved in 1 cc. benzene.)

Figure 4—Influence of 1,3,5-Trinitrobenzene on the Viscosity of Benzene-Rubber Sols

in a similar manner as in the case of the third group accelerators described in a previous paper (No. 1). The results of the experiments are shown in Figs. 1 to 4.

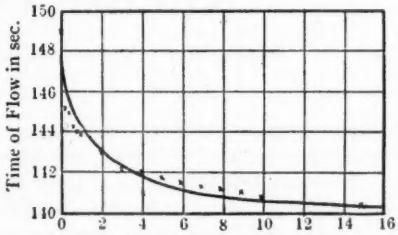
2. The change in viscosity with increasing proportions of vulcanizing agent was examined in detail, and it was found that increasing proportions of benzoyl peroxide and of the aromatic nitro compounds produce progressively increasing reductions in viscosity of rubber sols, as shown in Figs. 5–6.



(Viscosity measurements were conducted after one hour was allowed to elapse.)

Milligrams per 10 cc. of 0.4% rubber solution. (Acetone-extracted rubber used and benzoyl peroxide was added after dissolved in 1 cc. benzene.)

Figure 5—The Change of Viscosity with Increasing Amount of Benzoyl Peroxide



(Viscosity measurements were conducted after one hour was allowed to elapse.)

Milligrams per 10 cc. of 0.4% rubber solution. (1,3,5-Trinitrobenzene was added after dissolved in 1 cc. benzene.)

Figure 6—The Change of Viscosity with Increasing Amount of Trinitrobenzene

3. The rate of reduction of viscosity produced by Ostromislenski's vulcanizing agents can be expressed in the following formula, as in the case of the third group accelerators:

$$\eta_{i_0} - \eta_i = k. \log t;\ k = a + bt$$

where η_{i_0} is the viscosity of a rubber solution without addition of a vulcanizing agent and η_i is the same as η_{i_0}, except that the rubber solution is allowed to stand for t minutes after the addition of the vulcanizing agent.

4. From the observations above it is concluded that the lowering effect on the viscosity of rubber sols of Ostromislenski's vulcanizing agents, particularly benzoyl peroxide, mono-, di-, and trinitrobenzene, should be regarded as due to the combined actions of depolymerization, in other words, a breaking-up of the rubber molecules and a chemical reaction of the depolymerized rubber molecules with vulcanizing agents.

[Reprinted from Researches of the Electrotechnical Laboratory of the Ministry of Communications, Japanese Government, Tokyo, Japan. Research Paper No. 341.]

Studies on the Combined Action of Organic Accelerators for Rubber Vulcanization

Shukusaburo Minatoya, Kitaro Kojima, and Izumi Nagai

Synopsis

Keeping pace with recent developments in the rubber industry in general, various organic accelerators of good quality have been invented one after another, nearly one hundred different kinds of them being now put on the market. Though most of these accelerators, even when used singly, are satisfactory for regulating the time of vulcanization and improving the quality of vulcanizates, the combined use of two accelerators has come to be the subject of rubber chemists interested in this field, in order to obtain more efficient results on vulcanization. Thiollet and Martin (*Caout.*, **26**, 14,494 (1929)) and W. Norris (*Ind. Rubber World*, **82**, No. 2, 535 (1930)) have already published the results of experiments on the combined effect of organic accelerators, and state that in vulcanization they behave in a different manner from any single accelerators used separately. In these investigations, however, rather impure chemicals on the market were incorporated in rubber stocks, and only in arbitrary proportions, regardless of the proportions corresponding to their chemical constitutions.

Under the presumption that any two accelerators, if they are mixed *in a certain definite ratio*, may produce some remarkable effects, the present authors have studied the combined action of several accelerators on the market on the basis of the eutectic curves which they show when melted together. After locating the positions of the molecular compound and the eutectic mixtures on a eutectic curve obtained by measuring the melting point of two mixed accelerators, the authors first determined the mixing ratios corresponding to the same molecular compound and eutectic mixtures.

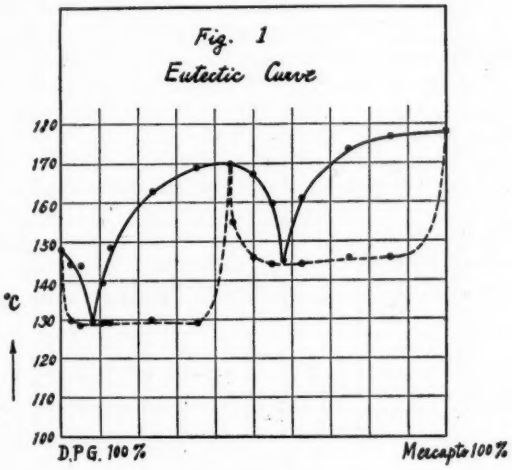
The behavior during vulcanization of the combined accelerators with the mixing ratios thus determined is the subject of the present authors' experiments, which covered the following four combinations:

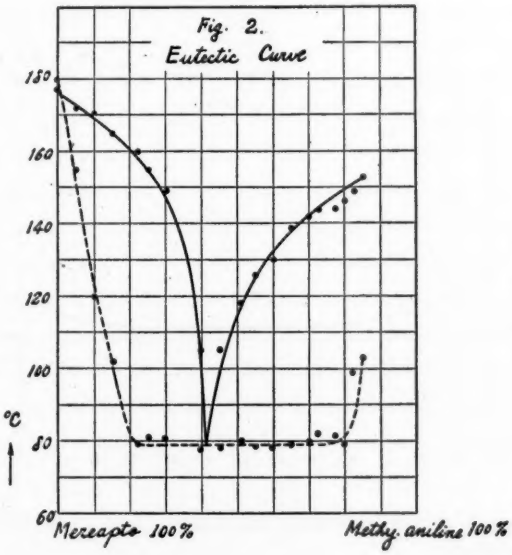
(*A*) Mercaptobenzothiazole and diphenylguanidine.
(*B*) Mercaptobenzothiazole and methylene-aniline.
(*C*) Tetramethylthiuram monosulfide and diphenylguanidine.
(*D*) Tetramethylthiuram disulfide and diphenylguanidine.

The eutectic curves were obtained by plotting the points measured by Rheinboldt's method (*Z. prak. Chem.*, **2**, 111, 242 (1925); 112, 187, 199 (1926)), *viz.*, after two purified, finely powdered materials were mixed in various proportions and placed in a capillary tube in an ordinary melting point measuring apparatus, two points were determined in each case for the various proportions, *i. e.*, one where fusion began and the other, where it was complete.

Experiments on the scorching tendency were carried out as follows. The test-pieces consisting of standard smoked sheet 100 parts, zinc oxide 100 parts, sulfur 3 or 5 parts, and 1 part of a single accelerator or combined one, were heated for 150 minutes at a maximum of 70° C. and 100° C., each of them being taken out one by one at intervals of 10 minutes. The scorching tendency was estimated from the

contrary turbidity curves drawn by a modified method of Vogt (*Ind. Rubber World*, **65**, 347 (1922)) (for the combinations (*A*) and (*B*)), and a method newly devised by the present authors (for the combinations (*C*) and (*D*)). In the latter method, instead of observations by the naked eye, the turbidity of benzine solutions was





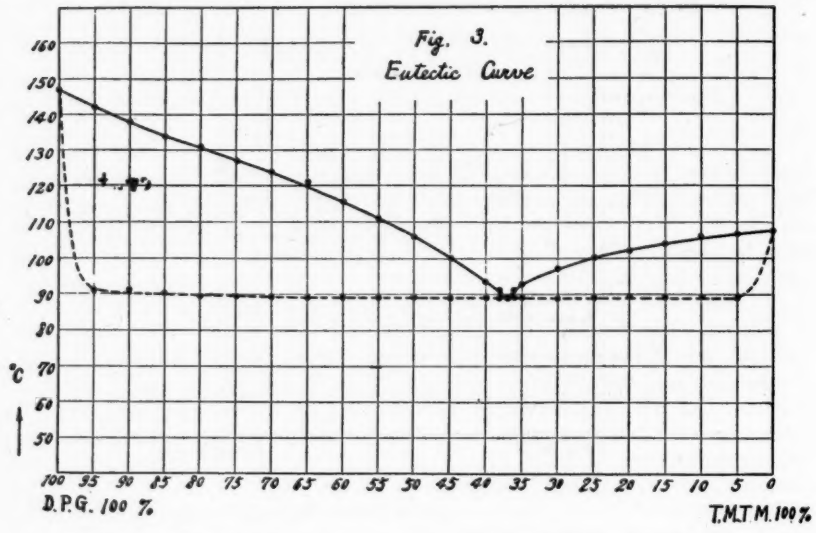
indicated by the deflection of a galvanometer connected with a cuprous oxide photoelectric cell.

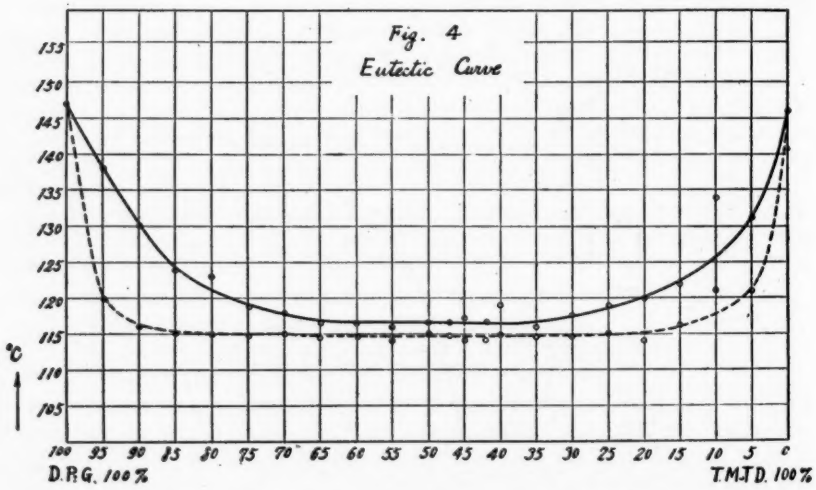
The tests of vulcanization were carried out under 45 and 20 lbs. per sq. in. (for the combinations (*A*) and (*B*)) and 10 lbs. per sq. in. (for the combinations of (*C*) and

(*D*)) steam pressures, with mixings consisting of standard smoked sheet 100 parts, zinc oxide 5 or 10 parts, sulfur 3 or 5 parts, accelerator 0.5 or 1 part.

From these experiments the following facts have been confirmed conclusively by the present authors.

1. In combination (*A*) one molecular compound and two eutectic compounds





were formed, each of which, especially the former, promotes both scorching and vulcanization strikingly.

2. In combination (*B*) only one eutectic compound is formed, and no molecular compound. The scorching tendency, though comparatively slight in all tests gradually increases with the increase in the proportion of mercaptobenzothiazole relative to diphenylguanidine. The accelerating effect on vulcanization is improved

by using the combined accelerator and reaches maximum at the eutectic point.

3. In combination (*C*), as in the case of (*B*), only one eutectic compound is formed. The scorching tendency and accelerating action increase remarkably by the combination, but do not reach a maximum at the eutectic point. The maximum point is attained in the neighborhood of tetramethylthiuram monosulfide 30%, diphenylguanidine 70%.

4. In combination (*D*) the eutectic curve is not distinct, so that it is impossible to determine the points of the molecular compound and eutectic mixtures. In spite of this, the scorching tendency and accelerating action are greatly increased by the combination, as in the case of (*C*), reaching a maximum near the point of tetramethylthiuram disulfide 30%, diphenylguanidine 70%.

5. The reason why the maximum activity is reached in the neighborhood of thiuram 30% and diphenylguanidine 70% in both the (*C*) and (D) combinations seems to be explained by the assumption that tetramethylthiuram monosulfide and disulfide are reduced by hydrogen sulfide, evolved during vulcanization, to dimethyldithiocarbamic acid, which combines with diphenylguanidine to form a molecular compound remarkably active in its scorching tendency and accelerating power.

[Translated for RUBBER CHEMISTRY AND TECHNOLOGY from Kautschuk, Vol. 9, No. 2, pages 18–20, February, 1933.]

A Method for Measuring Quantitatively the Swelling of Vulcanized Rubber in Organic Liquids by Means of a Voluminometer

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Introduction

The swelling of rubber has been studied extensively by many investigators, and the most important methods used to measure swelling quantitatively will be briefly mentioned here.

The method of direct weighing, in which the weight of the swelling liquid absorbed is determined, has been used by Hofmeister,[1] Flusin,[2] Kirchhof,[3] and Salkind.[4] Reinke[5] used a volumetric method, where, however, the swelling substance had to overcome a pressure. He measured two factors, first the increase in volume of the substance (absorption of liquid), and secondly the excess pressure which is in equilibrium with this increase. Posnjak[6] has extended this method further, and has devised an ingenious apparatus whereby the increase in volume of the swollen substance is determined by measuring the quantity of mercury displaced by the swelling. Here also swelling takes place under pressure which, within definite limits, can be changed at will.

Dubosc[7] has used, besides the method of direct weighing, a method which he calls "voluminometric," though it is not really voluminometric. He measured the change in length of a sample placed in the swelling liquid and calculated from this the increase in volume, on the assumption that the per cent changes are the same in all three dimensions.

In his very interesting investigation on swelling, Scott[8] used the gravimetric method, and calculated the per cent increase in volume of the sample.

In an anonymous paper on the effect of solvents on vulcanized rubber,[9] it is evident that the investigator determined the changes in volume of disc-shaped testpieces by measuring the diameter and the thickness.

Disadvantages of the Methods Used

There are certain disadvantages in the method of direct weighing to determine the increase in volume. Kirchhof[10] for instance has already pointed out certain shortcomings. Salkind[11] considers the method "not very precise," and says that errors of two to five per cent are to be expected, depending on the volatility of the swelling liquid.

The necessary calculations may easily lead to errors. As is known, part of the swollen rubber or the added fillers, such as bitumen, may be dissolved in the liquid, and this may lead to false results.

The voluminometric method of Posnjak is not suitable for a series of measurements, because swelling takes place in the measuring apparatus itself, and this can hold only one sample. Furthermore, the apparatus cannot be used by an untrained person.

The objection to the Dubosc method for examining commercial rubber articles is that changes are actually not the same in all directions. Moreover, this method has the disadvantages of the Posnjak method already mentioned.

Finally, the method of measuring the diameter and thickness should be considered very inaccurate. It is not even possible to use this method if the swelling progresses so far that the outer surface of the sample becomes jelly-like and the edges become badly defined.

In addition, all these methods of measurement are very time-consuming.

Description of the Voluminometer

Because the Dutch Rubber Institute was occupied with practical determinations

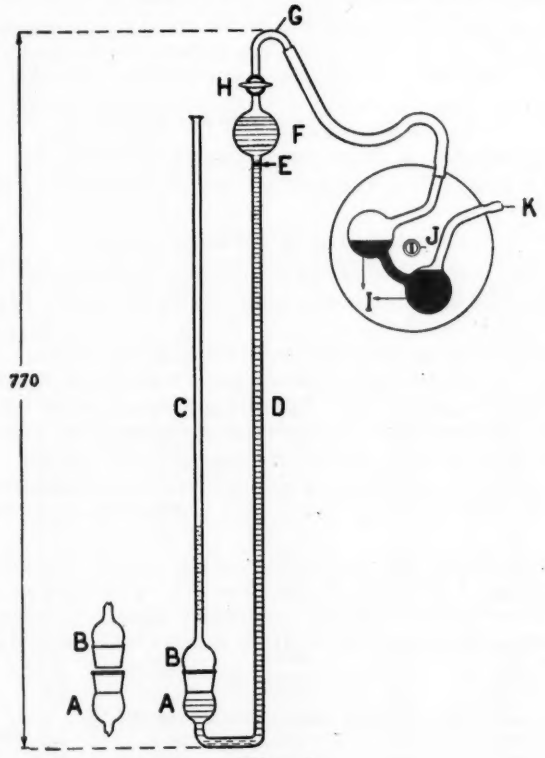

Figure 1

of swelling of rubber goods of the so-called oil-resistant type, the problem arose of devising a simple apparatus which should meet the following requirements:

1. The volume of the swelling or swollen sample must be read directly with the apparatus.
2. The apparatus must serve only to measure the volume, and the swelling of the sample must take place in small flasks in a thermostat.
3. The liquid used for measuring in the apparatus must be the same as the liquid used for swelling.
4. The difference between two determinations must not exceed 0.01 cc.
5. The procedure must be the simplest possible.

After a few preliminary experiments, a voluminometer was developed like that shown diagrammatically in Fig. 1.

Method of Filling with the Liquid

The measuring liquid is poured into bulb *A* and carried over to bulb *F* by suction on the rubber tube leading from the pump until *F* is nearly full, when stopcock *H* is closed. The pump is then turned to the right (clockwise) until the mercury completely fills the right bulb and rises two to three centimeters in tube *K* in addition. The left bulb should then be about one-quarter full. The rubber tube is then connected to the pump so that when *H* is opened *A* is closed by means of *B*. The measuring liquid is raised or lowered at will in *A*, *B*, and *C* by turning the pump.

The bulb *A* for holding the sample to be measured can be closed by means of a ground glass stopper, *B*, to which a calibrated glass tube *C*, graduated in 0.01 cc. units, is fused. The bulb *A* is connected with bulb *B* by a glass tube *D*. The diameters of *C* and *D* are the same. About one centimeter below bulb *F*, tube *D* has a mark *E*. The bulb *F* is connected with the double bulb *C* (called the pump in the text) by means of a curved connecting tube *G* (with stopcock *H*). The double bulb *I* is partly filled with mercury, and is arranged so it can be rotated around axis *J*.

Operation of the Voluminometer

The measurement of the volume of a substance is done in the following way: Stopcock *H* is opened, and the pump is turned to the left until bulb *F* is empty and the meniscus in *D* is exactly at mark *E*. The height of the liquid in *C* is then read. The pump is turned to the right until the liquid in *A* is about 0.5 centimeter below the lower edge of the stopper, the stopper is removed, the substance is placed in *A*, and the latter is again closed. By turning the pump to the left, the meniscus in *D* is again brought exactly to *E*, after which the height of the liquid in *C* is again read. The difference between the two readings gives the volume.

The measurement of the volume of a sample can be accomplished within three minutes from the time of taking it out of the swelling liquid and the subsequent immersion.

If very volatile liquids are used, a little of the liquid is lost by evaporation during the opening of the flask *A*. However, the quantity lost is very slight. If desired, this can be determined and a correction made. With benzine the average loss in practical determinations at 20° C. is 0.015 cubic centimeter.

TABLE I

CONTROL OF THE APPARATUS AT 20° C.

Determination	Reading	Volume in Cc.	Correction in Cc.[a]	Corrected Volume in Cc.	Deviation in Cc. from Volume Determined in Water
1	3.265				
	2.015	1.250		1.265	+0.002
2	3.340				
	2.095	1.245		1.260	−0.003
3	3.410				
	2.160	1.250	0.015	1.265	+0.002
4	3.640				
	2.390	1.250		1.265	+0.002
5	3.735				
	2.490	1.245		1.260	−0.003

[a] Average correction for benzine (see text).

Control of the Apparatus

The apparatus was controlled by measuring the volume of a small steel cylinder. By weighing it in distilled water, its volume was found to be 1.263 cubic centimeters. The apparatus was then filled with benzine. The results are given in Table I.

This control experiment showed that the precision of the apparatus was 0.005 cubic centimeter. The agreement between individual determinations met all requirements.

Representative Tests

As practical examples of the results obtained with the apparatus, two series of determinations are shown, which were made on samples 11.3 mm. in diameter and 5 mm. thick from the following mixture:

First latex crepe	100 parts
Zinc oxide	3
Diphenylguanidine	1
Sulfur	5

Vulcanized 20 and 30 min. at 147° C.

The swelling was carried out in benzine in a thermostat at 20° and 30° C., respectively. The measurements, likewise in benzine, were made at 20° C.

TABLE II

INCREASE IN VOLUME IN PER CENT OF THE ORIGINAL VOLUME

Measured after a Swelling Time of	Vulcanized 20 minutes			Vulcanized 30 minutes		
	1st Determination	2nd Determination	Average Value	1st Determination	2nd Determination	Average Value
Swelling Temperature 20° C.						
6 Hours	280	282	281	235	232	234
1 × 24	412	410	411	343	331	337
2 × 24	438	442	440	349	338	344
5 × 24	454	448	451	369	358	364
8 × 24	478	477	478	386	376	381
12 × 24	506	506	506	421	417	419
16 × 24	543	536	540	463	462	463
20 × 24	602	[a]	602	552	540	546
25 × 24	663		663	606	696	601
30 × 24	726		726	647	640	644
Swelling Temperature 30° C.						
6 Hours	292	292	292	260	262	261
1 × 24	468	467	468	376	376	376
2 × 24	492	490	491	382	382	382
5 × 24	561	567	564	402	404	403
8 × 24	645	690	668	442	434	438
12 × 24	810	860	835	504	498	501
16 × 24	980	1030	1005	587	572	580

[a] On account of lack of care in manipulation this sample broke into small pieces.

In the determination of the volumes after swelling, the liquid adhering to the samples was first carefully removed with filter paper. The results showed that the swelling of these vulcanizates at 20° C. could be continued up to thirty days and still have the measurements sufficiently precise. With longer swelling the measurements became inaccurate because the surface of the rubber became jelly-like and very soft. At 30° C., swelling had to be stopped for special reasons after sixteen days. It is however possible that this could be continued to twenty-five days without the precision of the measurements being too unfavorably affected.

The measurements are given in Table II, and are shown in graphical form in Figs. 2 and 3.

These results, as well as the results of many other measurements, agree with those published by Scott,[1] and show the same characteristic swelling curves. A comparison of Figs. 2 and 3 shows distinctly the influence of the temperature of swelling, which is obviously considerably greater for the mixture vulcanized 20 minutes than for that vulcanized 30 minutes.

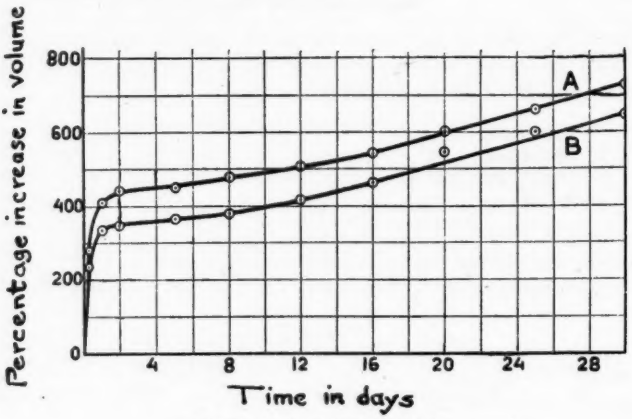

Figure 2—Swelling at 20° C.

A = Vulcanized 20 min. B = Vulcanized 30 min.

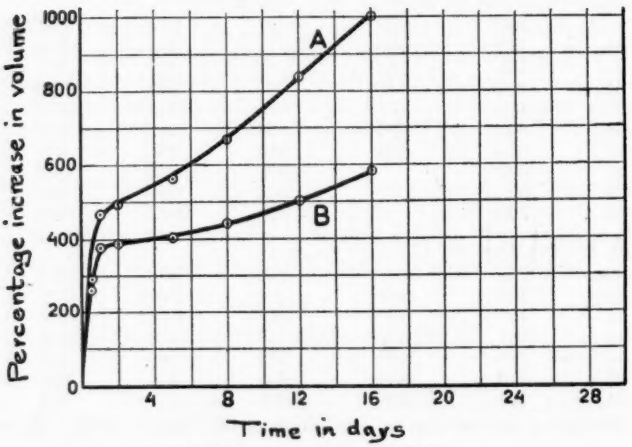

Figure 3—Swelling at 30° C.

A = Vulcanized 20 min. B = Vulcanized 30 min.

In conclusion it should be mentioned that the voluminometer described is used almost daily in the Dutch Rubber Institute to study the swelling of the so-called oil-resistant types of rubber, where not only has its usefulness been proved, but there is a greater precision and desirable saving of time in contrast to the older methods of measurement.

It may be stated further that the use of the apparatus is not limited to studying

the swelling of rubber in benzine. Swelling phenomena of other substances in various liquids may be investigated with the help of this apparatus, *e. g.*, wood in water, gelatin, artificial silk, and other materials of a like character.

Summary

1. A voluminometer for the study of the swelling of rubber is described, which may also be used for other substances, *e. g.*, wood, gelatin, artificial silk, and similar materials.

2. The advantages of this apparatus are:

(*a*) Swelling determinations with satisfactory precision can be carried out over longer periods of time than is the case with ordinary methods.

(*b*) The accuracy of the apparatus is greater than with the direct weighing method or with direct dimensional measurements.

(*c*) The procedure is extremely simple and rapid.

3. Typical results of practical swelling determinations at 20° C. and 30° C. are shown. The swelling curves derived from the data obtained agree with the investigations by Scott.[1]

The author thanks Dr. A. van Rossem, Director of the Institute, for his valuable advice and very helpful criticism.

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The Volumetric Determination of Free Sulfur

A. Castiglioni

In order to determine free sulfur in substances like rubber and antimony sulfide, extraction is carried out with a solvent, preferably acetone. After separation from the solvent, the extracted sulfur is converted into the sulfate and weighed as barium sulfate. With the object of making this determination easier and simpler, it occurred to the author to determine the sulfur in the acetone extract volumetrically, instead of gravimetrically, by utilizing the observed fact that potassium thiocyanate is formed when the acetone extract is boiled with potassium cyanide.

Experimental investigation of this subject showed that in the presence of an excess of potassium cyanide, conversion of the sulfur into potassium thiocyanate is quantitative, so that after evaporation of the solvent a mixture of potassium cyanide and potassium thiocyanate remains behind. To determine the potassium thiocyanate in the aqueous solution of these two salts, the method of Schulek (cf. *Z. anal. Chem.*, **65**, 433 (1924–25)) was used, which is based on the decomposition of potassium cyanide by formaldehyde. Instead, however, of adding an excess of titrated silver nitrate solution, as recommended by Schulek, and then determining the excess silver by the Volhard method, the titration was carried out directly with the silver nitrate solution, using iron nitrate as indicator, until the blood-red color of ferric thiocyanate had disappeared. In the following table are given the results of determinations by this procedure.

Sulfur (Weighed) in Grams	Sulfur (Found) in Grams	Difference in Grams
0.0716	0.07132	−0.00028
0.2899	0.2868	−0.0031
0.1417	0.1411	−0.0006
0.1002	0.09973	−0.0029
0.1384	0.1368	−0.0016

In these determinations known quantities of sulfur were used. Although compared with the gravimetric determination this method is more convenient and more rapid, it gives sufficiently precise results.

The procedure can be carried out in the following way. Boil the acetone extract for 0.5 hour with an excess of potassium cyanide in a round flask with a reflux condenser, and evaporate the solvent on a water bath. Dissolve the dried residue in about 100 cc. of water, place it in a 200-cc. flask, add 10 cc. of 20 per cent formaldehyde soln., and agitate carefully. Acidify with 5 cc. of 30 per cent nitric acid and fill to the mark with water. Remove individual portions of 20 cc. of the liquid, and add 5–6 drops of 10 per cent iron nitrate solution, whereupon the liquid turns an intense blood-red color. Upon titration with a 0.05 normal silver nitrate solution a white precipitate of silver thiocyanate is formed, and the red color becomes weaker until it disappears completely, while in many cases it changes to a light bluish color. Since silver thiocyanate tends to agglomerate into cheesy masses which may contain some of the liquid to be analyzed so that the latter cannot be acted upon by the silver nitrate, the silver nitrate must be dropped slowly from the burette and the liquid must be kept in agitation during the titration. The various

samples of the liquid make it possible to determine the required number of cubic centimeters of silver nitrate solution required for complete precipitation of the silver thiocyanate which is present. This value multiplied by $\left(10 \times \frac{S}{AgNO_3}\right) = 1.8877$ and by the factor of the solution gives the sulfur content of the acetone extract which is analyzed.

Further investigation is in progress upon the possibility of applying this method to other analyses, such as the qualitative detection of traces of sulfur or of cyanides.